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SUPPLEMENT TO MELLOR'S
COMPREHENSIVE TREATISE ON
INORGANIC AND THEORETICAL CHEMISTRY

VOLUME VIII
SUPPLEMENT I
N (Part I)

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

By J. W. Mellor, D.Sc., F.R.S.

Vol. I.	H, O.
Vol. II.	F, Cl, Br, I, Li, Na, K, Rb, Cs.
Vol. III.	Cu, Ag, Au, Ca, Sr, Ba.
Vol. IV.	Ra and Ac Families, Be, Mg, Zn, Cd, Hg.
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Vol. XI.	Te, Cr, Mo, W.
Vol. XII.	U, Mn, Ma, and Re, Fe (Part I).
Vol. XIII.	Fe (Part II).
Vol. XIV.	Fe (Part III), Co.
Vol. XV.	Ni, Ru, Rh, Pd, Os, Ir.
Vol. XVI.	Pt and general index.

SUPPLEMENTS

Vol. II.	Supp. I.	F, Cl, Br, I, At.
	Supp. II.	Li, Na.
	Supp. III.	K, Rb, Cs, Fr.
Vol. VIII.	Supp. I.	N (Part I).

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Supplement to
MELLOR'S COMPREHENSIVE
TREATISE ON

INORGANIC AND THEORETICAL CHEMISTRY

Prepared under the direction
of an Editorial Board

VOLUME VIII

SUPPLEMENT I

Nitrogen (Part I)

LONGMANS

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PREFACE

On occasion a chemist may find it necessary to embark on an exhaustive study of the information now available on a certain topic, and to ascertain precisely by what steps it has been acquired, evaluated and understood. In these days of increasingly rapid extension of chemical knowledge he will not lightly undertake such a task, for it requires him personally to analyse indexes of abstract literature, to trace the original sources of the facts, discussions and theories the existence of which is thereby disclosed, and to examine with care all those sources, whether original papers, treatises, books or patent specifications, which may be accessible to him. Such labours may extend over many weeks or months, and it will therefore occasion no surprise if he prefers to rely, in the first instance at any rate, on a detailed review such as is provided by the original volumes of Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry" and the corresponding Supplements which from time to time are published.

The present supplementary volume offers a review of the chemistry of nitrogen and ammonia, gathering together, examining and arranging in a convenient manner the information that has become available since the publication of the original Treatise, and indicating clearly the sources of such information. The contributors have brought to their tasks specialized knowledge of, and interest in, their prescribed range of subject matter, and hence the Editors have been content to leave to their judgment the breadth and depth of their consideration of the various matters at issue. In a work of this character there must of necessity be some selection, and in this respect the Editors have offered only general guidance, believing that the specialist contributors are in the best position to discriminate, disregarding some material as trivial or irrelevant, and dealing at some length with other more significant aspects of the subject. Nevertheless all have endeavoured to ensure that by consulting this Supplement together with the appropriate volume of the original Treatise any chemist, particularly if his interests are in the inorganic or physical areas of the subject, should readily obtain a clear and reasonably complete picture of useful knowledge in the topics treated, while at the same time he is offered in generous measure quantitative data expressed in tabulated numerical or in graphical form and (ideally at any rate) both the original source of every statement and its reference in "Chemical Abstracts". Equally it is hoped that biochemists, spectrochemists, radiochemists, some organic chemists, and chemists concerned with the production of chemical materials will find in these Supplements most of the important information to which they would expect to have ready access, and the relevant sections (except in respect of organic reactions and the finer technological points of manufacturing processes) have therefore been prepared with the same attention to detail as have those concerned, for example, with the physico-chemical properties of individual compounds.

Of the ammonium salts only the halides, sulphide, sulphate, carbonate, nitrate and phosphate are considered here; other ammonium salts have been, or will be, treated in the Supplements dealing with the acids from which they are derived.

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ACKNOWLEDGMENTS

INEVITABLY the preparation or supplementation of a large work of reference is an increasingly complex task, requiring the closest integration of effort among those who establish and record scientific facts and those who present them to their readers. In these days of extensive publication in many languages the interpretation and presentation of the information usually involve a chain of authors, reviewers, and abstractors who all need to work with mutual appreciation and understanding. All those who have shared in the preparation of this Supplement have therefore a duty to express their indebtedness to people who, by their lucid presentation, informed criticism or accurate analysis of the scientific subject matter considered herein, have rendered possible a task that, in its present scope and form, would otherwise have been beyond the powers of the Contributors and Editors to perform. It has been their aim to acknowledge clearly the source of every significant statement, quoting the original author's name and the reference both to the original paper and to the abstract of that paper in "Chemical Abstracts".

The Editors also desire to express their appreciation of the effective way in which the Contributors have readily responded to their suggestions and requests. Although the Editors have endeavoured to supply abstracts of all relevant papers for their consideration, access to the libraries of academic and scholastic institutions and to the Science Library, South Kensington, and the library of the Patent Office has from time to time afforded valuable information the examination of which might otherwise have been difficult. Imperial Chemical Industries Ltd., through its Billingham and Alkali Divisions, has again supported the project of supplementation of Mellor's "Comprehensive Treatise" both by encouragement and also by affording facilities to certain contributors in their study of published information. For similar reasons warm thanks are also offered to the British Oxygen Co., Ltd., the North Thames Gas Board, Messrs. Fisons Ltd. and the Gas Council, London.

Once again the Editors welcome an opportunity to acknowledge the advice and help always offered in generous measure by Messrs. Longmans, Green & Co., Ltd. and to express both to the Company and to individual members of its staff their appreciation of this happy co-operation.

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page 517, fig. 2 from *J.A.C.S.*, published by the American Chemical Society. Page 64, fig. 4 from *I.U.P.A.C. and Inst. Mech. Eng. Joint Conf.*, published by the Institution of Mechanical Engineers. Page 73, fig. 6 from *J. Chem. Phys.*, published by the American Institute of Physics. Page 156, figs. 1, 2; pages 174–5, figs. 15–18; pages 180–1, figs. 21, 22; pages 187–8, figs. 24, 25; pages 205–6, figs. 32–4 from *J. Electrochem. Soc.* Page 172, figs. 7, 8 from *J. Inst. Metals.* Pages 219–20, figs. 45, 46 from *J. Iron & Steel Inst.*, both published by the Institute of Metals. Page 171, fig. 6; pages 173–4, figs. 9–14; pages 178–9, figs. 19, 20; pages 190–1, figs. 26, 27; pages 193–4, figs. 28, 29; page 198, fig. 30; page 216, fig. 42 from *J. Metals, AIME Trans.*, published by AIME. Page 88, fig. 18 from *J. phys. Chem.*, American Chemical Society. Pages 82–5, figs. 10–15 from *J. Res. Nat. Bur. Stand.* Page 15, fig. 7 from *Philips Technical Review*, published by Philips Electrical, Ltd. Page 44, fig. 2 from *Phys. Rev.* Page 216, fig. 43; pages 221–3, figs. 47–50; page 230, fig. 63 from *Proc. Roy. Soc. A.* Page 524, fig. 3 from *Rec. Trav. Chim.*, published by the Royal Netherlands Chemical Society. Pages 225–6, figs. 54–6 from *Sci. Repts. Res. Inst. Tohuku Univ.* Pages 168–9, figs. 3–5 from *Trans. Am. Soc. Metals.* Page 87, fig. 17 from *Trans. Faraday Soc.* Page 217, fig. 44 from *Trans. Indian Inst. Metals.* Page 86, fig. 16 by permission of the Union Carbide International Company, New York. Page 186, fig. 23 from *Z. anorg. Chem.*, published by Johann Ambrosius Barth. Page 202, fig. 31; page 460, fig. 1 from *Z. physik. Chem.*, published by Akademische Verlagsgesellschaft Geest & Portig K.-G., Leipzig. Pages 211–13, figs. 36–41 from *Z. Elektrochem.*, published by Verlag Chemie, G.m.b.H., Weinheim. Page 81, fig. 9; page 101, fig. 22; pages 111–12, figs. 32, 33; page 517, fig. 1; page 260, fig. 1 from *Ind. Eng. Chem.*, published by the American Chemical Society. Page 264, fig. 2 by permission of the Tennessee Valley Authority: pages 265–6, figs. 3, 4 by permission of the Montecatini General Mining and Chemical Corporation and the Commercial Solvents Corporation: all three figures from *Chem. Eng. Prog.*, published by the American Institute of Chemical Engineers.

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ABBREVIATIONS

absolute	abs.
alternating current	a.c.
ampère-s	amp.
Ångstrom unit-s	A.
atmosphere-s (after a numeral)	atm.
atomic weight	at. wt.
boiling point	b.p.
British thermal unit-s	B.Th.U.
Calorie-s (large)	kg.-cal. or kcal.
calorie-s (small)	g.-cal.
centimetre-s	cm.
cubic centimetre-s	c.c.
density (with a numeral)	ρ, *d*
direct current	d.c.
electromotive force	e.m.f.
foot, feet	ft.
freezing point	f.p.
gram-s (with a numeral)	g.
hour-s (with a numeral)	hr.
inch-es	in.
kilogram-s	kg.
kilowatt-s	kW.
litre-s (with a numeral)	l.
melting point	m.p.
milliampère-s	ma.
millilitre-s	ml.
millivolt-s	mV.
minute-s	min.
molecular weight	mol. wt.
parts per million	p.p.m.
potential difference	p.d.
second-s (time only)	sec.
specific gravity	sp. gr.
square centimetre-s	sq. cm.
vapour density	v.d.
vapour pressure	v.p.
volt-s	V.
watt-s	W.
wave-length	λ

LIST OF LITERATURE ABBREVIATIONS

The following list of Journal titles includes all those referred to in Volume II, Supplements 1, 2 and 3, and in the present Supplement if information additional to the abbreviation employed in the reference lists is available. For uniformity, the literature abbreviations used in the references are the same as in *An Advanced Treatise on Physical Chemistry* by J. R. Partington. Where a source is cited which does not appear in that work, the abbreviation is that currently used by Chemical Abstracts. In many cases further information, e.g. concerning change of title, period of publication, etc., will be found in the lists of titles of periodicals published from time to time by the American Chemical Society in Chemical Abstracts. Information concerning location is also given in the World List of Scientific Periodicals.

Arsberetning vedkommende Norges Fiskerier. Bergen.

Abh. Deut. Kältetech. Ver. Abhandlungen des deutschen kältetechnischen Vereins. Karlsruhe.

Abhl. Akad. Munich. Abhandlungen der mathematisch-physikalischen Klasse der Königlichen Bayerischen Akademie der Wissenschaften. Munich.

Abhl. Braunschweig. Wiss. Ges. Abhandlungen der braunschweigischen wissenschaftlichen Gesellschaft.

Abhl. Ges. Wiss. Gött. Abhandlungen der Königlichen Gesellschaft der Wissenschaften zu Göttingen. Mathematisch-physikalische Klasse. Göttingen.

Abhl. K. Akad. Berlin. Abhandlungen der Kgl. Akademie der Wissenschaften zu Berlin. Physikalisch-mathematische Klasse. Berlin.

Abhl. Naturwiss. Verein Hamburg. Abhandlungen aus dem Gebiete der Naturwissenschaften. Herausgegeben vom Naturwissenschaftlichen Verein in Hamburg. Hamburg.

Abhl. Preuss. Akad. Wiss. Math. Klasse. Abhandlungen der preussichen Akademie der Wissenschaften, Mathematisch-naturwissenschaftliche Klasse. Berlin.

Abhl. Sächs. Akad. Abhandlungen der Königlichen Sächsischen Akademie der Wissenschaften zu Leipzig. Mathematisch-physische Klasse. Leipzig.

Abstracts Bact. Now Biological Abstracts, Philadelphia.

Abstr. Comm. 1st Intern. Congr. Biochem. International Congress of Biochemistry, 1st Congress, Cambridge, England, 1949. Abstracts of Communications.

Abstr. Japan. Chem. Lit. Abstracts of Japanese Chemical Literature.

Abstr. Roy. Soc. Abstracts of Papers Communicated to the Royal Society of London. London.

Acad. Rep. Populare Romîne. Academia republicii populare Romîne, Filiala Iaşi, Studii şi cercetări ştiinţifice. Bucharest.

Acad. Română Mem. sect. stiint. Academia Română Memoriile secţiunii ştiinţifice. Bucharest.

Acad. Tchèque Sci., Bull. Intern., Classe Sci. Math. Nat. Med. Academie tchèque des sciences, Bulletin international, Resumés des travaux presentés, Classe des sciences, mathematiques, naturelles, et de la médecine.

Acero y Energia (Barcelona). Barcelona.

Acker- u. Pflanzenbau (see *Z. Acker- u. Pflanzenbau*).

Acta Acad. Aboensis Math. Phys. Acta Academiae Aboensis, Mathematica et Physica. Abö. Finland.

Acta Adriat. Acta Adriatica. Split, Yugoslavia.

Acta Agr. Scand. Acta Agriculturae Scandinavica. Stockholm.

Acta Agral. Fennica. Acta Agralia Fennica. Helsinki.

Acta Agron. Acta Agronomica. Palmira, Columbia.

Acta Chem. Scand. Acta Chemica Scandinavica. Copenhagen.

Acta Chim. Acad. Sci. Hung. Acta Chimica Academiae Scientiarum Hungaricae. Budapest.

Acta Comment. Univ. Dorpatensis. Acta et Commentationes Universitatis Dorpatensis. Dorpat (Yuriev or Jurjeff).

Acta Cryst. Acta Crystallographica. London.

Acta Endocrinol. Acta Endocrinologica. Copenhagen.

Acta Gastro-Enterol. Belg. Acta Gastro-Enterologica Belgica.

Acta Lit. Sci. Reg. Univ. Hung. (See *Acta Univ. Szeged*) Acta Litterarum ac Scientiarum Regiae Universitatis Hungaricae Francisco-Josephinae. Szeged, Hungary.

Acta Math. Acta Mathematica. Stockholm.
Acta Med. Philippina. Acta Medica Philippina. Manila.
Acta Med. Scand. Acta Medica Scandinavica. Stockholm.
Acta Metallurgica. London.
Acta Orthopaed. Scand. Acta Orthopaedica Scandinavica. Copenhagen.
Acta Path. Microbiol. Scand. Suppl. Acta Pathologica et Microbiologica Scandinavica. Copenhagen.
Acta Phys. Austriaca. Acta Physica Austriaca. Vienna.
Acta Phys. Acad. Sci. Hung. Acta Physica Academiae Scientiarum Hungaricae. Budapest.
Acta Phys. Polon. Acta Physica Polonica. Warsaw.
Acta Physicochim. U.R.S.S. Acta Physicochimica U.R.S.S. Moscow.
Acta Physiol. Acad. Sci. Hung. Acta Physiologica Academiae Scientiarum Hungaricae. Budapest.
Acta Physiol. Scand. Acta Physiologica Scandinavica. Stockholm.
Acta Phytochim. (Japan). Acta Phytochimica (Japan). Tokyo.
Acta Radiol. Acta Radiologica. Stockholm.
Acta Soc. Sci. Fenn. Acta Societatis Scientiarum Fennicae. Helsinki.
Acta Univ. Asiae Mediae. Acta Universitatis Asiae Mediae. Tashkent, U.S.S.R.
Acta Univ. Latviensis. Acta Universitatis Latviensis. Riga.
Acta Univ. Szeged, Chem. et Phys. Acta Universitatis Szegediensis, Sectio Scientiarum Naturalium, Acta Chemica et Physica. Szeged, Hung.
Acta Univ. Voron. Acta Universitatis Voronegiensis. Voronezh, U.S.S.R.
Acustica. Stüttgart.
Adv. in Biol. and Med. Phys. Advances in Biological and Medical Physics, New York, London.
Adv. in Chem. Advances in Chemistry Series. New York.
Adv. in Enzymol. Advances in Enzymology. New York.
Adv. in Modern Biol. (*U.S.S.R.*). Advances in Modern Biology. Moscow.
A.E.C.D. Atomic Energy Commission Documents.
A.E.R.E., Reports. Atomic Energy Research Establishment, Reports.
Aeronaut. Eng. Rev. Aeronautical Engineering Review. Easton, Pa.
Afinidad. Barcelona.
Agrártudomány. (*Agricultural Science*). Budapest.
Agr. Chem. Agricultural Chemicals. Baltimore.
Agriculture. Ministry of Agriculture. London.
Agr. Gaz. N.S. Wales. Agricultural Gazette of New South Wales. Sydney.
Agr. J. of India. Agricultural Journal of India. Delhi.
Agr. & Live-stock in India. Agriculture and Live-stock in India.
Agricultura. Louvain. Belgium.
Agricultura Coloniale. Florence.
Agr. Res. Inst. Pusa, Sci. Repts. Agricultural Research Institute of Pusa, Scientific Reports.
Agrokemia. Budapest.
Agron. J. Agronomy Journal. Madison, Wis.
A.I. Ch. E. Journal. American Institute of Chemical Engineers Journal. New York.
A.I.M.E. Trans. American Institute of Metallurgical Engineers, Transactions. New York.
Air Repair. Pittsburgh, Pa.
Aircraft Eng. Aircraft Engineering. London.
Akad. Nauk. S.S.S.R. Akademiya Nauk S.S.S.R. Moscow.
Akad. Nauk Ukr. S.S.R., Inst. Teploenerg. Sb. Tr. Akademiya Nauk U.S.S.R., Institut Teploenergetiki, Sbornik Trudov.
Akust. Z. Akustische Zeitschrift. Leipzig.
Alabama Agr. Expt. Sta. Alabama Polytechnic Institute, Agricultural Experiment Station. Auburn, Alabama.
Alembic Club Reprint. Alembic Club Reprints. Edinburgh.
Allg. Brauer u. Hopfenzeit. Allgemeine Brauer- und Hopfenzeitung.
Allg. Öl u. Fettztg. Allgemeine Öl- und Fettzeitung. Vienna.
Allgem. Forstz. Allgemeine Forstzeitschrift. Munich.
Allgem. Wärmetechnik. Zeitschrift für Wärme-, Kälte- und Verfahrenstechnik. Frankfurt a.M.
Aluminium. Düsseldorf.
Aluminium (*Budapest*).
Aluminium Non-Ferrous Rev. Aluminium and the Non-Ferrous Review. London.
Am. Dyestuff Reptr. American Dyestuff Reporter. New York.
Amer. Brewer. American Brewer. New York.
Amer. Ceram. Soc. Bull. American Ceramic Society Bulletin. Columbus. Ohio.

Amer. Chem. Abstr. Chemical Abstracts. Published by the American Chemical Society. Easton, Pa.
Amer. Chem. J. American Chemical Journal. Baltimore.
Amer. Doc. Inst. American Documentation Institute. Washington.
Amer. Fertilizer. American Fertilizer. Philadelphia.
Amer. Foundryman. American Foundryman. Chicago.
Amer. Gas J. American Gas Journal. Dallas.
Amer. Heart J. American Heart Journal. St. Louis.
Amer. Inst. Chem. Eng. American Institute of Chemical Engineers. New York.
Amer. Inst. Min. Met. Eng. Contrib. American Institute of Mining and Metallurgical Engineers. Contributions. New York.
Amer. Inst. Min. Met. Eng. Techn. Publ. American Institute of Mining and Metallurgical Engineers. Technical Publication. New York.
Amer. Inst. Min. Met. Eng. Met. Div. Techn. Pub. American Institute of Mining and Metallurgical Engineers. Metallurgical Division. Technical Publication. [Journal of Metals. New York.
Amer. J. Botany. American Journal of Botany. New York.
Amer. J. Cancer. American Journal of Cancer.
Amer. J. Clin. Pathol. American Journal of Clinical Pathology. Baltimore.
Amer. J. Dental Res. American Journal of Dental Research. St Louis.
Amer. J. Diseases Children. American Journal of Diseases of Children. Chicago, Illinois.
Amer. J. Hyg. American Journal of Hygiene. Baltimore.
Amer. J. Math. Phys. American Journal of Mathematics, Pure and Applied. Cambridge, Mass.
Amer. J. Med. American Journal of Medicine. New York.
Amer. J. Med. Sci. American Journal of the Medical Sciences. Philadelphia.
Amer. J. Obstet. Gynecol. American Journal of Obstetrics and Gynecology. St. Louis.
Amer. J. Ophthalmol. American Journal of Ophthalmology. Chicago, Illinois.
Amer. J. Orthodontics etc. American Journal of Orthodontics and Oral Surgery.
Amer. J. Pharm. American Journal of Pharmacy. Philadelphia.
Amer. J. Phys. American Journal of Physics. New York.
Amer. J. Physiol. American Journal of Physiology. Washington.
Amer. J. Pub. Health. American Journal of Public Health. New York.
Amer. J. Roentgen. American Journal of Roentgenology. Springfield, Illinois.
Amer. J. Sci. American Journal of Science. New Haven, Conn.
Amer. J. Surg. American Journal of Surgery. New York.
Amer. J. Trop. Med. American Journal of Tropical Medicine. Baltimore.
Amer. Machinist. American Machinist. New York. [Also a London edition, with supplement.]
Amer. Min. The American Mineralogist. Menasha, Wis.
Amer. Perfumer. (See *Amer. Perfumer Essent. Oil Rev.*)
Amer. Perfumer Essent. Oil Rev. American Perfumer and Essential Oil Review. Bristol, Conn.
Amer. Potato J. American Potato Journal. New Brunswick, N.J.
Amer. Rocket Soc. J. American Rocket Society Journal. New York.
Amer. Ry. Eng. Assoc. Bull. American Railway Engineering Association Bulletins. Chicago.
Amer. Scientist. American Scientist. New Haven, Conn.
Amer. Soc. Metals. American Society for Metals. Cleveland, Ohio.
Amer. Soc. Refrig. Eng. J. American Society of Refrigerating Engineers Journal. New York.
Amer. Soc. Testing Mat. Bull. American Society for Testing Materials. Bulletin. Philadelphia.
Amer. Soc. Testing Mat. Radiography Symposium. American Society for Testing Materials. Symposium on Radiography and *X*-Ray Diffraction Methods. Philadelphia, 1937.
An. Acad. Brasil. Cienc. Anais da Academia Brasileira de Ciencias. Rio de Janeiro.
An. Acad. Roman. Mem. Sti. Analele Academiei Româna. Memoriile Secţ. Ştiinţifice. Bucharest.
An. Asoc. Quim. Argentina. Anales de la Asociación Quimica Argentina. Buenos Aires.
An. Asoc. Quim. Farm. Uruguay. Anales de la Asociación de Quimica y Farmacia del Uruguay. Montevideo.
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An. Facult. Quim. Farm. Anales de la Facultad de Quimica y Farmacia. Montevideo.
An. Farm. Bioquim. Anales de Farmacia y Bioquimica. Buenos Aires.

An. Fis. Quim. Anales de la Real Sociedad Española de Fisica y Quimica. Madrid. [Now divided into A, Physics and B, Chemistry].

An. I. Congr. Pan-Amer. Ing. Minas y Geol. Santiago Chile. Anales del congreso panamericano de ingenieria de minas y geologia, 1st. Congress. Santiago.

An. Inst. Med. Exptl. Valencia. Anales del instituto de medicina experimental de Valencia.

An. Ofic. Quim. Prov. Buenos Aires. Anales de la oficina quimica de la provincia. (La Plata).

An. Quim. Farm. Anales de Quimica y Farmacia. Santiago, Chile.

An. Real. Acad. Farm. Anales de la Real Academia de Farmacia. Madrid.

An. Real. Soc. Espan. Fis. Quim. Anales de la real sociedad española de fisica y quimica. Madrid.

An. Soc. Cient. Argentina. Anales de la Sociedad Cientifica Argentina. Buenos Aires.

An. Soc. Españ. Fis. Quim. Anales de la Sociedad Española de Fisica y Quimica. Madrid.

Anal. Chem. See *Ind. Eng. Chem. Anal.*

Anal. Chim. Acta. Analytica Chimica Acta. Houston, Tex., London, Amsterdam.

Analyst. The Analyst. Cambridge.

Anat. Record. Anatomical Record. Philadelphia.

Anesthesiology. Journal of the American Society of Anesthesiologists. Philadelphia, Pa.

Anesthesia and Analgesia. Cleveland, Ohio.

Angew. Bot. Angewandte Botanik. Berlin-Zehlendorf.

Angew. Chem. Angewandte Chemie. Leipzig.

Anilinokrasochnaya Prom. Anilinokrasochnaya Promyshlennost. Moscow.

Ann. (*Ann. Chem.*). Annalen der Chemie. [Liebig's Annalen]. Weinheim.

Ann. Acad. Brasil. Sci. Annaes da Academia Brasileira de Sciencias. Rio de Janeiro.

Ann. Acad. Sci. Fenn. Annales Academiae Scientiarum Fennicae. Helsinki.

Ann. Acad. Sci. Tech. Varsovie. Annales de l'Académie des Sciences Techniques à Varsovie. Warsaw.

Ann. Agr. Coll. Sweden. (See *Kgl. Lantbrucks-Högskolans Ann.*).

Ann. Agron. Annales Agronomiques. Paris.

Ann. Appl. Biol. Annals of Applied Biology. Cambridge.

Ann. Astrophys. Annales d'astrophysique. Paris.

Ann. Biol. Clin. Paris. Annales de Biologie Clinique. Paris.

Ann. Botany (*London*). Annals of Botany. London.

Ann. Chim. Annales de Chimie. Paris. [Formerly combined with Annales de Physique as Annales de Chimie et de Physique].

Ann. Chim. Anal. Appl. Annales de Chimie Analytique et de Chimie Appliquée. Paris.

Ann. Chim. Appl. Annali di Chimica Applicata. Rome.

Ann. Chim. Phys. Annales de Chimie et de Physique. Paris.

Ann. Chim. Rome. Annali di chimica. Rome.

Ann. Combustibles Liquides. Annales de l'Office National des Combustibles Liquides. Paris.

Ann. de l'Ecole Norm. Annales Scientifiques de l'Ecole Normale Supérieure. Paris.

Ann. de Phys. Annales de Physique. Paris. [See *Ann. Chim.*].

Ann. Dermatol. Syphil. Annales de Dermatologie et de Syphiligraphie. Paris.

Ann. des Ponts et Chaussées. Annales des Ponts et Chaussées. Paris.

Ann. Ecole Nat. Agr. Montpellier. Annales de l'École Nationale d'Agriculture de Montpellier. Montpellier.

Ann. Endocrinol. (*Paris*). Annales d'endocrinologie. Paris.

Ann. Entomol. Soc. Amer. Annals of the Entomological Society of America. College Park, Ma.

Ann. Ergzb. Annalen der Chemie Ergänzungsbände. [See *Ann.*].

Ann. Fac. Sci. Marseille. Annales de la Faculté des Sciences, Université de Marseille.

Ann. Fac. Sci. Toulouse. Annales de la Faculté des Sciences, Université de Toulouse. Toulouse.

Ann. Fac. Sci. Univ. Toulouse, Sci. Math. et Sci. Phys. Annales de la faculté des sciences de l'université de Toulouse pour les sciences mathematiques et les sciences physiques. Paris.

Ann. Fals. Annales des Falsifications et des Fraudes. Paris.

Ann. Gembloux. Annales de Gembloux. Belgium.

Ann. Géophys. Annales de Géophysique. Paris.

Ann. Inst. Anal. Phys. Chim. Annales de l'Institut d'Analyse Physico-chimique. Moscow.

Ann. Inst. Hydrol. et Climatol. Annales de l'Institut d'Hydrologie et de Climatologie. Paris.

Ann. Inst. Mines Leningrad. Annales de l'Institut Mines. Leningrad.

Ann. Inst. Natl. Recherche Agron. Annales de l'Institut National de la Recherche Agronomique. Paris.

Ann. Inst. Pasteur. Annales de l'Institut Pasteur. Paris.

Ann. Intern. Med. Annals of Internal Medicine. Philadelphia.

Ann. Ist. Super. Agrar. Portici. Annali del r. Istituto Superiore Agrario del Portici.

Ann. Mat. Pura ed Applicata. Annali di Mathematica Pura ed Applicata. Milan, Bologna.

Ann. Med. Leg. Crim. Police Sci. Med. Soc. Toxicol. Annales de Médecine Légale de Criminologie, Police Scientifique, Médecine Sociale et Toxicologie. Paris.

Ann. Mines. Annales des Mines. Paris. [A continuation of Journal des Mines].

Ann. New York Acad. Sci. Annals of the New York Academy of Sciences. New York.

Ann. Pharm. Franç. Annales Pharmaceutiques Françaises. Paris.

Ann. Phil. Annals of Philosophy. London.

Ann. Phys. Annalen der Physik. Leipzig. [Several series, each with a separate volume number sequence; formerly Annalen der Physik und Chemie, etc. Sometimes quoted as Poggendorff's Annalen, Wiedemann's Annalen, Drude's Annalen, with the name of the Editor].

Ann. Phys. Beibl. Beiblätter zu den Annalen der Physik (1881-1919). Leipzig. [Continued as *Phys. Ber.*].

Ann. Phys. Boltzmann Festschr. Ludwig Boltzmann Festschrift Gewidmet. Leipzig. 1904. [Uniform with the volumes of Annalen der Physik].

Ann. Phys. Ergzb. Annalen der Physik Ergänzungsbände. [See *Ann. Phys.*].

Ann. Phys. Pogg. Jubelband. Annalen der Physik. Poggendorff Jubelband. Berlin, 1874. [See *Ann. Phys.*].

Ann. Postes, Teleg. Teleph. Annales des Postes, Télégraphie et Téléphonie.

Ann. Rep. Alkali etc., Works. Annual Report on Alkali etc., Works. London.

Ann. Rep. Chem. Soc. Annual Reports of the Chemical Society. London.

Ann. Rep. E. Malling Res. Sta. Annual Report, East Malling Research Station, Maidstone.

Ann. Rep. Mich. Acad. Sci. Annual Report of Michigan Academy of Science.

Ann. Rep. N.Y. State Assoc. Milk Sanitarians. Annual Report of the New York State Association of Milk Sanitarians. New York.

Ann. Rep. Progr. Chem. Annual Reports on the Progress of Chemistry. London.

Ann. Rep. Smithsonian Inst. Smithsonian Institute Reports. Washington.

Ann. Rept. Intern. Assoc. Milk Sanitarians. Annual Report of the International Association of Milk Sanitarians. New York.

Ann. Rev. Biochem. Annual Review of Biochemistry. Stanford, Calif.

Ann. Rev. Microbiol. Annual Review of Microbiology. Stanford, Calif.

Ann. Rev. Nucl. Sci. Annual Review of Nuclear Science. Stanford, Calif.

Ann. Rev. Phys. Chem. Annual Review of Physical Chemistry. Stanford, Calif.

Ann. Sci. Annals of Science. London.

Ann. Sci. Agron. (*Ann. Agron.*). Annales de la science agronomique française et étrangère.

Ann. Sci Univ. Jassy. Annales Scientifique de l'Université de Jassy. Jassy, Rumania.

Ann. Sect. Anal. Phys. Chim. Inst. Chim. Gén. U.R.S.S. Annales du Secteur d'Analyse Physico-Chimique. Institut de Chimie Générale, U.R.S.S. Moscow.

Ann. Soc. Geol. Belg. Annales de la Société Géologique de Belgique. Bulletin. Liège.

Ann. Soc. Sci. Bruxelles. Annales de la Société Scientifique de Bruxelles. Louvain.

Ann. Sper. Agrar. (*Rome*). Annali della Sperimentazione Agraria. Rome.

Ann. Staz. Sper. Agrar. Annali della r. stazione sperimentale agraria di Modena. Modena, Italy.

Ann. Surg. Annals of Surgery. Philadelphia.

Ann. Univ. Mariae-Curie-Sklodowska Lublin-Polonia. Annales Universitatis Mariae-Curie-Sklodowska. Lublin, Poland.

Ann. Univ. Sofia (*phys. math.*). Annuaire de l'Université de Sofia. Faculté Physico-Mathématique. Sofia.

Annali di Chimica. Annali di Chimica e Storia Naturali. Rome.

Annuar. Regia Staz. Chim. Agrar. Torino. Annuario della Regia Stazione Chimica Agraria in Torino. Turin.

Antibiotics and Chemotherapy. Washington.

Anz. Akad. Wiss. Wien. (See *Österr. Akad. Wiss.*). Anzeiger der Akademie der Wissenschaften in Wien, Mathematisch-naturwissenschaftliche Klasse. Vienna.

Anz. Schädlingskunde. Anzeiger für Schädlingskunde. Hamburg.

Apotheker Ztg. Apothekerzeitung. Berlin.

Apparatebau. Hanover.

Appl. Microbiol. Applied Microbiology. Baltimore.

Appl. Sci. Res. Applied Scientific Research. The Hague.

Aptechnoe Delo. (Pharmaceutical Transactions.) Moscow.

Arb. dritt. Abt. anat. Inst. kaiser. Univ. Kyoto. Arbeiten aus der dritten Abteilung des anatomischen Institutes der kaiserlichen Universität Kyoto.

Arb. K. Wilhelm Inst. Kohlenforsch. Arbeiten des Kaiser-Wilhelm Instituts für Kohlenforschung in Mühlheim-Ruhr. Berlin.

Arb. Kais. Ges. Arbeiten aus dem kaiserlichen Gesundheitsamte.
Arb. Med. Univ. Okayama. Arbeiten aus der Medizinischen Fakultät, Universität Okayama, Japan.
Arb. Reichsgesund. Arbeiten aus dem Reichsgesundheitsamte.
Arb. Staatl. Inst. Exptl. Therap. u. Forsch.-Inst. Chemotherap. Frankfurt. Arbeiten aus dem Staatlichen Institut für Experimentelle Therapie und dem Forschungs-Institut für Chemotherapie zu Frankfurt. Frankfurt a.M.
Arch. Biochem. Archives of Biochemistry. New York, London.
Arch. Biochem. Biophys. Archives of Biochemistry and Biophysics. New York, London.
Arch. di Fisiol. Archivio di Fisiologia. Florence.
Arch. Disease Childhood. Archives of Disease in Childhood. London.
Arch. 'E. Maragliano' Patol. e Clin. Archivio 'E. Maragliano' di Patologia e Clinica. Genoa.
Arch. Eisenhüttenw. Archiv für das Eisenhüttenwesen. Düsseldorf.
Arch. Elektrotech. Archiv für Elektrotechnik. Berlin.
Arch. Exp. Path. Pharm. Archiv für Experimentelle Pathologie und Pharmakologie. Berlin.
Arch. Farmacol. Sper. Archivio di Farmacologia Sperimentale e Scienze Affini. Rome.
Arch. Farm. Bioquim. Tucumán. Archivos de Farmacia y Bioquimica del Tucumán. Tucumán, Argentina.
Arch. Gartenbau. Archiv für Gartenbau. Berlin.
Arch. ges. Physiol. (Pflüger). Pflüger's Archiv für die gesamte Physiologie des Menschen und der Tiere. Berlin.
Arch. ges. Virusforsch. Archiv für die gesamte Virusforschung. Vienna.
Arch. ges. Wärmetech. Archiv für die gesamte Wärmetechnik. Frankfurt a.M.
Arch. Gewerbepath. Gewerbehyg. Archiv für Gewerbepathologie und Gewerbehygiene.
Arch. Hydrobiol. Archiv für Hydrobiologie. Stuttgart.
Arch. Ind. Health. Archives of Industrial Health.
Arch. Ind. Hyg. Occupational Med. Archives of Industrial Hygiene and Occupational Medicine. Chicago.
Arch. Inst. Cardiol. Mex. Archivos del Instituto de Cardiologie de Mexico. Mexico City.
Arch. Inst. Farmacol. Exptl. Archivos del Instituto de Farmacologie Experimental. Madrid.
Arch. Internal Med. Archives of Internal Medicine. Chicago.
Arch. Intern. Pharmacod. Archives Internationales de Pharmacodynamie et de Thérapie Ghent.
Arch. Intern. Physiol. Archives Internationales de Physiologie. Liège.
Arch. Ist. Biochim. Ital. Archivio dell'Istituto Biochimico Italiano.
Arch. Ital. Malattie Apparato Digerente. Archivio Italiano delle Malattie dell'Apparato Digerente. Bologna.
Arch. Klin. Chir., Langenbecks. Archiv für Klinische Chirurgie, Langenbecks. Berlin.
Arch. Lagerstättenforsch. Archiv für Lagerstättenforschung. Berlin.
Arch. Mat. Naturvidensk. Archiv for Mathematik og Naturvidenskab. Oslo.
Arch. Med. Interna. Havana. Archivos de Medicina Internale. Havana.
Arch. Metallkde. Archiv für Metallkunde. Berlin.
Arch. Mikrobiol. Archiv für Mikrobiologie. Berlin.
Arch. Mineralogiczne. Archiwum Mineralogiczne Towarzystwa Naukowego Warszawskiego. Warsaw.
Arch. Min. Soc. Sci. Varsovie. Archives de Mineralogie de la Société des Sciences de Varsovie. Warsaw.
Arch. Mus. Teyler. Archives du Musée Teyler. Haarlem.
Arch. Néerl. Archives Néerlandaises des Sciences Exactes et Naturelles. Leiden.
Arch. Néerl. Phys. Archives Néerlandaises de Physiologie de l'Homme et des Animaux. Leiden.
Arch. Neurol. Psychiatry. Archives of Neurology and Psychiatry. Chicago.
Arch. Ophthalmol. Archives of Ophthalmology. Chicago.
Arch. Ophthalmol., Graefe's. Archiv für Ophthalmologie vereinigt mit Archiv für Augenheilkunde, Albrecht von Graefe's. Berlin.
Arch. Otolaryngol. Archives of Otolaryngology. Chicago.
Arch. Pathol. Archives of Pathology. Chicago.
Arch. Pflanzenbau. Archiv für Pflanzenbau.
Arch. Pharm. Archiv der Pharmazie. Weinheim.
Arch. Pharm. Chemi. Archiv for Pharmaci og Chemi. Copenhagen.
Arch. Physiol. Archives de Physiologie Normale et Pathologique. Paris.
Arch. Phys. Biol. Archives de Physique Biologique. Paris.

Arch. Phys. Med. Rehabil. Archives of Physical Medicine and Rehabilitation. Chicago, Illinois.

Arch. Protistenk. Archiv für Protistenkunde.

Arch. Sci. (Geneva). Archives des Sciences (Geneva).

Arch. Sci. Biol., Italy. Archivio di Scienze Biologiche (Italy). Bologna.

Arch. Sci. Biol. U.R.S.S. Archives des Sciences Biologiques. Petrograd.

Arch. Sci. Med. Archivio per le Scienze Mediche. Turin.

Arch. Sci. Phys. Nat. Archives des Sciences Physiques et Naturelles. Geneva.

Arch. Sci. Physiol. Archives des Sciences Physiologiques. Paris.

Arch. Soc. Biol. Montevideo. Archivos de la Sociedad de Biologia de Montevideo. Montevideo.

Arch. Suikerind. Archief voor de Suikerindustrie in Nederlandsch-Indië. The Hague.

Arch. techn. Messen. Archiv für technisches Messen. Munich.

Arch. Venezolanos Nutric. Archivos Venezolanos de Nutricion. Caracas.

Arch. Wärmewirtsch. Archiv für Wärmewirtschaft. Berlin.

Archiv Gesch. Naturwiss. Technik. Archiv für die Geschichte der Naturwissenschaft und der Technik. Leipzig.

Arhiv Hem. Farm. Arhiv za Hemiju i Farmaciju. Belgrade.

Arhiv Kem. Arhiv za Kemiju. Zagreb.

Ariz. Bur. Mines, Mineral Technol. Bull. Arizona Bureau of Mines, Mineral Technology Bulletin.

Arkansas Agr. Expt. Sta. Bull. University of Arkansas Agricultural Experiment Station. Fayetteville, Ark.

Arkh. Biol. Nauk. Arkhiv Biologicheskikh Nauk. U.S.S.R.

Arkiv. Botan. Arkiv för Botani.

Arkiv Fys. Arkiv för Fysik. Uppsala.

Arkiv Kem. Arkiv för Kemi. Uppsala.

Arkiv Kem. Min. Geol. Arkiv för Kemi, Mineralogi och Geologi. Uppsala.

Arkiv Mat. Astron. Fys. Arkiv för Matematik, Astronomi och Fysik. Uppsala.

Arkiv Zool. Arkiv för Zoologi, utgivet av K. Svenska Vetenskapsakademien. Uppsala.

Army Ordnance. Washington.

Arquiv. Biol. e Tecnol., Inst. Biol. e Pesquisas Tecnol. Arquivos de Biologia e Tecnologia, Instituto de Biologia e Pesquisas Tecnologicas. Parana.

Arquiv. Inst. Biol. São Paulo. Arquivos do Instituto Biologica. São Paulo.

Assoc. Food Drug Officials U.S. Quart. Bull. Association of Food and Drug Officials of the United States. Quarterly Bulletin. Austin, Texas.

Assoc. Operative Millers. Association Operative Millers, Bulletin. Kansas City.

Assoc. Southern Agr. Workers. Association of Southern Agricultural Workers. New Orleans.

Assoc. Tech. Ind. Papetière Bull. Association Technique de l'Industrie Papetière, Bulletin. Paris.

Asphalt Teerind. Ztg. Asphalt und Teerindustrie Zeitung und Zeitschrift für Strassenbau, Strassenunterhaltung sowie Tief- und Bruckenbau.

A.S.T.M. Bull. American Society for Testing Materials Bulletin. Philadelphia.

Astron. J. Astronomical Journal. New York.

Astron. J. Soviet Union. Astronomical Journal of the Soviet Union. Moscow.

Astron. Zhur. Astronomicheskii Zhurnal. Moscow.

Astrophys. J. The Astrophysical Journal. Chicago.

Astrophys. Norvegica. Astrophysica Norvegica.

Ateneo Parmense. Parma.

Atm. Energ. S.S.S.R. Atomic Energy U.S.S.R.

Atomics Eng. and Technol. Atomics, Engineering and Technology. London.

Atti Accad. Catania. Atti della R. Accademia Gioenia di Scienze Naturali. Catania.

Atti. Accad. Ital. Fis. Mat. Atti della Reale Accademia d'Italia. Memorie della Classe di Scienze Fisiche, Matematiche e Naturali. Rome.

Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. e Nat. Atti della Accademia Nazionale dei Lincei, Rendiconti, Classe di Scienze Fisiche, Matematiche e Naturali. Rome.

Atti Congr. Naz. Chim. Ind. Atti del Congresso Nazionale di Chimica Industriale. Milan.

Atti Congr. Naz. Chim. Pura Applic. Atti del Congresso Nazionale di Chimica Pura ed Applicata. Rome.

Atti III Congr. Intern. Vetro, Venice. Atti del Congresso Internazionale del Vetro, 3rd Congress. Venice, 1953.

Atti Mem. Accad. Sci. Padova. Atti e memorie della regia accademia di scienze, lettere e arti di Padova. Padua.

Atti R. Accad. Lincei. Atti della Reale Accademia dei Lincei. Rendiconti. Classe di Scienza Fisiche, Matematiche e Naturali. Rome.

Atti R. Accad. Napoli. Atti della Reale Accademia delle Scienze Fisiche e Matematiche. Societa Reale di Napoli. Naples.

Atti R. Accad. Torino. Atti della Reale Accademia delle Scienze di Torino. Turin.

Atti R. Inst. Veneto. Atti del Reale Instituto Veneto di Scienze, Lettere ed Arti. Venice.

Atti Regia Accad. Fisiocrit. Siena. Atti della Regia Accademia dei Fisiocritici in Siena, Sezione Medico-Fisica. Siena.

Atti Soc. Nat. Mat. Modena. Atti della società dei naturalisti e matematici di Modena, Modena.

Atti X Congr. Intern. Chim. Atti del congresso internazionale di chimica, 10th Congress. Rome, 1938.

Australasian Engr. The Australasian Engineer. Sydney.

Australia Bur. Min. Res., Geol. and Geophys. Summary Rep. Australia, Bureau of Mineral Resources, Geology and Geophysica. Summary Reports. Canberra.

Australian Chem. Inst. J. and Proc. Australian Chemical Institute Journal and Proceedings.

Australian J. Agr. Res. Australian Journal of Agricultural Research. Melbourne.

Australian J. Appl. Sci. Australian Journal of Applied Science. Melbourne.

Australian J. Biol. Sci. Australian Journal of Biological Sciences. Victoria.

Australian J. Dairy Technol. Australian Journal of Dairy Technology. Melbourne.

Australian J. Exp. Biol. Med. Sci. Australian Journal of Experimental Biology and Medical Science. Adelaide.

Australian J. Sci. Australian Journal of Scientific Research. Series A. Physical Sciences. Melbourne.

Australian Pulp and Paper Ind. Tech. Assoc. Proc. Australian Pulp and Paper Industry, Technical Association Proceedings. Melbourne.

Autogene Metallbearbeit. Autogene Metallbearbeitung.

Avhl. Norsk. Videns. Akad. Oslo. Avhandlinger utgitt av det Norske Videnskaps-Akademie i Oslo. I. Matematisk-Naturvidenskapelig Klasse. Oslo.

Avtogennoe Delo. (Acetylene Welding). Moscow.

Avtomat. Svarka. Avtomaticheskaya Svarka (Automatic Welding) Kiev.

Avtomobil. i Traktor. Prom. Avtomobil'naya i Traktornaya Promyshlennost. Moscow.

Azerbaid. Neft. Khozy. Azerbaidzhanskoe Neftyanoe Khozyaistvo. Baku, U.S.S.R.

B.A.E.R. British Atomic Energy Reports.

Baking Technology.

B.A. Rep. British Association for the Advancement of Science. Reports. London.

B.A. Rep. Coll. Chem. Reports on Colloid Chemistry. British Association for the Advancement of Science. London.

Bauing. Der Bauingenieur. Berlin.

Beama J. The Beama Journal. London.

Bee World. London.

Beiheft Z. V. deut. Chem. Zeitschrift des Vereins deutscher Chemiker (Beiheft). [Formerly Zeitschrift für Angewandte Chemie]. Weinheim.

Beit. Pathol. Anat. u. Allgem. Pathol. Beiträge zur Pathologischen Anatomie und zur Allgemeinen Pathologie. Jena.

Beitr. Geophys. Gerlands Beiträge zur Geophysik. Leipzig.

Beitr. Klin. Tuberk. Beiträge zur Klinik der Tuberkulose. Berlin.

Beitr. Kryst. Min. Beiträge zur Krystallographie und Mineralogie. Heidelberg.

Beitr. Min. Petr. Beiträge zur Mineralogie und Petrographie. Berlin.

Bell Lab. Rec. Bell Laboratories Record. New York.

Bell Syst. Techn. J. Bell System Technical Journal. New York.

Bell Telephone Quart. Bell Telephone Quarterly. New York.

Bell Telephone Syst. Techn. Monogr. Bell Telephone System Technical Monographs. New York.

Bell Telephone Syst. Techn. Publ. Bell Telephone System Technical Publications. New York.

Ber. Berichte der Deutschen Chemischen Gesellschaft. Berlin.

Ber. D. botan. Ges. Berichte der Deutschen Botanischen Gesellschaft. Jena.

Ber. D. keram. Ges. Berichte der Deutschen keramischen Gesellschaft. Bad Honef/Rhein.

Ber. D. Phys. Ges. See *Z. Phys.*

Ber. ges. Physiol. exptl. Pharmakol. Berichte über die gesamte Physiologie und experimentelle Pharmakologie. Berlin.

Ber. Ges. Kohlentech. Berichte der Gesellschaft für Kohlentechnik. Dortmund.

Ber. Inst. Phys. Chem., Akad. Wiss. U.S.S.R. Berichte des Instituts für physikalische Chemie, Akademie der Wissenschaften der U.S.S.R. Kiev.

Ber. Nat. Med. Verein. Innsbruck. Berichte des naturwissenschaftlich-medizinischen Vereins in Innsbruck. Innsbruck.

Ber. Oberhess. Ges. Natur- u. Heilkde. Bericht der Oberhessischen Gesellschaft für Natur- und Heilkunde. Giessen.

Ber. Phys.-ökonom. Ges. Königsberg. Bericht über die in den Sitzungen der Physikalisch-ökonomischen Gesellschaft zu Königsberg in Pr. gehaltenen Vorträge. Königsberg.

Ber. Verhandl. Sächs. Akad. Wiss. Leipzig. Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig.

Ber. Verhl. Nat. Ges. Freiburg. Berichte über die Verhandlungen der Naturforschenden Gesellschaft zu Freiburg i. Br. Freiburg.

Beret. 18th Skand. Naturforskermode. Beretning om det Skandinaviske Naturforskermoede. 18th Meeting, Copenhagen, 1929.

Berg. u. Hütten. Monatsh. Berg- und hüttenmännische Monatshefte der montanistischen Hochschule in Leoben. Vienna.

Berg- und Hüttenmännisches Jahrb. Berg- und hüttenmännisches Jahrbuch der montanistischen Hochschule in Leoben. Vienna.

Bergbau. Bergbau Archiv. Essen.

Bergcultures. Bogor, Indonesia.

Bergm. J. Bergmännische Journal. Freiberg.

Berl. u. Münch. Tier. Woch. Berliner und Münchener tierärztliche Wochenschrift. Berlin-Friedenau.

Berlin Ber. Sitzungsberichte der [Königlichen] Preussischen Akademie der Wissenschaften. Physikalisch-Mathematische Klasse. Heidelberg.

Berlin. klin. Wochenschr. Berliner klinische Wochenschrift. Berlin.

Better Crops with Plant Food. Washington.

Bibl. Univ. Bibliothèque Universelle de Genève. Geneva.

Biedermann's Zentr. Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschaft. Berlin, Leipzig.

Bihang Kgl. Svensk. Vet. Akad. Handl. Bihang till Kongliga Svenska Vetenskaps-Akademiens Handlinger. Stockholm.

Biochem. J. The Biochemical Journal. Cambridge.

Biochem. J. (Ukraine). Biochemical Journal (Ukraine).

Biochem. Z. Biochemische Zeitschrift. Heidelberg.

Biochim. & Biophys. Acta. Biochimica et Biophysica Acta. Amsterdam.

Biochim. Terap. Biochimica e Terapia Sperimentale. Milan.

Biodynamica. Madison, Wis.

Biokhimiya. Moscow, Leningrad.

Biol. Abstr. Biological Abstracts. Philadelphia.

Biol. Bull. Biological Bulletin. Woods Hole, Mass.

Biol. Rev. Biological Reviews of the Cambridge Philosophical Society. Cambridge.

Biol. Zentr. Biologisches Zentralblatt. Leipzig.

Blast Furnace Steel Plant. Blast Furnace and Steel Plant. Pittsburg.

Bodas Oro Real Soc. Españ. Fís. y Quím. Crónica Actos Conmem. Conf. Gen. Coloquios y Ses. Cient., Madrid. Bodas de Oro de la Real Sociedad Española de Física y Química. Crónica de los Actos Conmemorativos Conferencias Generales Coloquios y Sesiones Cientificas, Madrid.

Bodenkultur. Vienna.

Bodenkunde u. Pflanzenernähr. Bodenkunde und Pflanzenernährung.

Bol. Acad. Cienc. Argentina. Boletin de la Academia Nacional de Ciencias de la Republica Argentina. Córdoba.

Bol. Acad. Cienc. Exactas (Mad). Boletin de la Academia de Ciencias Exactas, Fisicas y Naturales (Madrid).

Bol. Acad. Nacl. Cienc. Córdoba. (See *Bol. Acad. Cienc. Argentina*).

Bol. Assoc. Brasil. Met. Boletim da Associação Brasileira de Metais. São Paulo.

Bol. Inst. Españ. Oceanog. Boletin del Instituto Español de Oceanografia. Madrid.

Bol. Inst. Geol. Espãna. Boletin del instituto geologico y minero de Espãna. Madrid.

Bol. Inst. Med. Exptl. Estud. Cancer, Buenos Aires. Boletin del Instituto de Medicina Experimental para el Estudio y Tratamiento del Cancer, Buenos Aires.

Bol. Inst. Nacl. Invest. Agron. (Madrid). Boletin del Instituto Nacional de Investigaciones Agronimicas. Madrid.

Bol. Min. Soc. Nacl. (Chile). Boletin minero (Sociedad Nacional de Mineria, Santiago, Chile). Santiago.

Bol. Obras. Sanit. Nacion. Boletin de Obras Sanitarias de la Nación. Buenos Aires.

Bol. Ofic. Asoc. Tecn. Cuba. Boletin Oficial del Asociación de Técnicos Azucareros. Havana, Cuba.

Bol. Soc. Biol. Santiago Chile. Boletin de la Sociedad de Biologia de Santiago de Chile. Santiago.

Bol. Soc. Chilena Quim. Boletin de la Sociedad Chilena de Quimica. Concepción.

Bol. Soc. Nacl. Min. Boletin de la Sociedad Nacional de Mineria del Peru. Lima.

Bol. Soc. Quim. Peru. Boletin de la Sociedad Quimica del Peru. Lima.

Boll. Accad. Catania. Bollettino delle Sedute dell'Accademia Gioena di Scienze Naturali in Catania. Catania.

Boll. Chim. Farm. Bollettino Chimico Farmaceutico. Milan.

Boll. Ist Super. Agrar. Pisa. Bollettino dell'istituto superiore agrario di Pisa.

Boll. Lab. Chim. Prov., Bologna. Bollettino dei Laboratori Chimici Provinciali (Bologna).

Boll. Laniera. Bollettino della Laniera. Rome.

Boll. Oculist. Bolletino d'Oculistica. Bologna, New York.

Boll. Sci. Fac. Chim. Ind. Bologna. Bollettino Scientifico della Facoltà di Chimica Industriale dell'Università di Bologna. Bologna.

Boll. Soc. Eustachiana. Bollettino della Società Eustachiana degli Istituti Scientifici dell'Università di Camerino. Camerino.

Boll. Soc. Geol. Ital. Bollettino della Società Geologica Italiana. Rome.

Boll. Soc. Ital. Biol. Sper. Bollettino della Società Italianà di Biologia Sperimentale. Naples.

Boll. Staz. Pato. Vegetale. Bollettino della Stazione di Patologia Vegetale. Rome.

Boll. Tec. Regio Ist Sper. Colt. Tabacchi 'Leonardo Angeloni', Scafati. Bollettino Tecnico del Regio Istituto Sperimentale per la Coltivazione dei Tabacchi 'Leonardo Angeloni', Scafati. Rome.

Bombay Technol. Bombay Technologist. Bombay.

Bot. Abstr. Botanical Abstracts. Philadelphia.

Bot. Gaz. Botanical Gazette. Chicago.

Bot. Zhur. Botanicheskii Zhurnal. Moscow.

Botan. Arch. Botanisches Archiv. Leipzig.

Botan. Mag. Tokyo. The Botanical Magazine (Tokyo). Tokyo.

Botan. Rev. Botanical Review. New York.

B.P. British Patent.

Bragantia. São Paulo.

Brandschutz. Stuttgart.

Brasil, Dept. Nacl. Produção Mineral, Bol. Brazil, Ministério da Agricultura, Departamento Nacional da Produção Mineral Boletin. Rio de Janeiro.

Brasseur Franç. Le Brasseur Français.

Braunkohle. Düsseldorf.

Braunkohlenarch. Das Braunkohlenarchiv, Vorkommen-Gewinnung-Verarbeitung-Verwendung der Brennstoffe. Halle.

Brennstoff-Chem. Brennstoff-Chemie. Essen.

Brennstoff- u. Wärmewirtsch. Brennstoff und Wärmewirtschaft. Halle.

Brennstoff-Wärme-Kraft. Düsseldorf, Germany.

Brit. Assoc. Adv. Sci. Rep. British Association for the Advancement of Science Report of the Annual Meeting. London.

Brit. Cast Iron Res. Assoc. Journal. Birmingham.

Brit. Chem. Abstr. British Abstracts. Bureau of Abstracts. London.

Brit. Chem. Eng. British Chemical Engineering. London.

Brit. Clayworker. The British Clayworker. London.

Brit. Heart J. British Heart Journal. London.

Brit. J. Appl. Phys. British Journal of Applied Physics. London.

Brit. J. Exp. Path. British Journal of Experimental Pathology. London.

Brit. J. Ind. Med. British Journal of Industrial Medicine. London.

Brit. J. Nutrition. British Journal of Nutrition. Cambridge.

Brit. J. Ophthalmol. British Journal of Ophthalmology. London.

Brit. J. Pharmacol. British Journal of Pharmacology and Chemotherapy. London.

Brit. J. Phot. British Journal of Photography. London.

Brit. J. Radiol. British Journal of Radiology. London.

Brit. Med. Bull. British Medical Bulletin. London.

Brit. Med. J. British Medical Journal. London.

Brit. Stand. Specif. British Standard Specification. British Standards Institution. London.

Brown Boveri Rev. The Brown Boveri Review. Baden, Switzerland.

B.S.I. British Standards Institution. London.
Buisseiron Kenkyû. Osaka, Japan.
Bul. Cultivar. Fermentar. Tutunului. Buletinul Cultivarii si Fermantarui Tutunului. Bukarest.
Bul. Fac. Stiinte Cernăuti. Buletinul Facultătii de Ştiinţe din Cernăuti.
Bul. Sci. Fak. Terkultura. Bulteno Scienca de la Fakultato Terkultura, Kjusu Imperia Universitato, Fukuoka, Japan.
Bul. Soc. Chim. Roman. Buletinul Societăţii de Chimie (din România). Bukarest.
Bul. Soc. Român. de Stiinte. Buletinul de Chimie Pură si Applicată, Societăţea Română de Ştiinţe. Bukarest.
Bul. Soc. Stiinte Cluj. Buletinul Societătii de Ştiinţe din Cluj. Cluj, Rumania.
Bul. Soc. Stiinte Farm. Roman. Buletinul de Societătii Ştiinţe e Farmacia Române.
Bul. Stiinte Fiz. Soc. Română Stiinte. Buletinul de Ştiinţe Fizica Pure si Aplicate, Societăţea Română de Ştiinţe.
Bulgar. Akad. Nauk. Otdel. Geol.-Geograf. i Khim. Nauki, Izvest. Khim. Inst. Bulgarska Akademiya na Naukite, Otdelenie za Geologo-Geografski i Khimicheski Nauki, Izvestiya na Khimicheskiya Institut. Sofia.
Bull. Acad. Med. Bulletin de l'Académie de Médecine. Paris.
Bull. Acad. Polon. Bulletin Internationale de l'Académie Polonaise des Sciences et Lettres. Section A. Cracow.
Bull. Acad. Romaine. Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Acad. Roy. Belg. Bulletin de l'Académie Royale de Belgique. Classe des Sciences. Brussels.
Bull. Acad. Sci. Georgian S.S.R. Bulletin of the Academy of Sciences of the Georgian S.S.R.
Bull. Acad. Sci. Russe. Bulletin de l'Academie des Sciences de Russie. Leningrad.
Bull. Acad. Sci. U.R.S.S. Bulletin de l'Academie des Sciences de l'Union des Républiques Soviétiques Socialistes. Moscow.
Bull. Acad. Sci. Union Rep. Sov. Soc. Classe Sci. Phys.-Math. Bulletin de l'Académie des Sciences de l'Union des Républiques Sovietiques Socialistes. Classe des Sciences.
Bull. Acad. Sci. (U.P.) Agra & Oudh. Bulletin of the Academy of Sciences of the United Provinces of Agra and Oudh, Allahabad, India.
Bull. Acad. St. Petersb. Bulletin de l'Academie Imperiale des Sciences de St. Petersburg. St. Petersburg.
Bull. Amer. Assoc. Petroleum Geol. Bulletin of the American Association of Petroleum Geologists. Tulsa, Okla.
Bull. Amer. Ceram. Soc. Bulletin of the American Ceramic Society. Columbus, Ohio.
Bull. Amer. Meteorol. Soc. Bulletin of the American Meteorological Society. Boston.
Bull. Amer. Phys. Soc. Bulletin of the American Physical Society. New York.
Bull. Assoc. Chim. Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie de France et des Colonies. Paris.
Bull. Assoc. Chim. Sucr. Dist. Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie et des Industries Agricoles de France et des Colonies.
Bull. Assoc. Franç. Tech. Pétrole. Bulletin de l'Association française des Techniciens du Pétrole. Paris.
Bull. Biol. Med. Exptl. U.R.S.S. Bulletin de Biologie et de Médecine Experimentale de l'U.R.S.S. Moscow.
Bull. Brit. Soc. Hist. Sci. Bulletin of the British Society for the History of Science. London.
Bull. Centr. Res. Inst. Univ. Travancore. Bulletin of the Central Research Institute, University of Travancore. India.
Bull. Central Electrochem. Res. Inst., Karaikudi. Bulletin of the Central Electrochemical Research Institute. Karaikudi. India.
Bull. Centre Belge Étude et Document. Eaux, Liège. Bulletin du Centre Belge d'Étude et de Documentation des Eaux. Liège.
Bull. Chem. Res. Inst. Non-aq. Solns., Tohôku Univ. Bulletin of the Chemical Research Institute of Non-aqueous solutions, Tohôku University. Japan.
Bull. Chem. Soc. Japan. Bulletin of the Chemical Society of Japan. Tokyo.
Bull. Chungking Inst. Ind. Res. Bulletin of Chungking Institute of Industrial Research, Ministry of Industry and Commerce. Chungking, China.
Bull. Classe Sci. Acad. Roy. Belg. Bulletin de la Classe des Sciences, Académie Royale de Belgique. Brussels.
Bull. Comm. Geol. Finlande. Bulletin de la Commission Géologique de Finlande. Helsinki.
Bull. Ecole Polytechn. Jassy. Bulletin de l'École Polytechnique de Jassy. Jassy, Rumania.
Bull. Electrotech. Lab. (Tokyo). Bulletin of the Electrotechnical Laboratory. Tokyo.

Bull. Eng. Expt. Stat. Univ. Illinois. University of Illinois. Engineering Experiment Station. Bulletin. Urbana, Ill.
Bull. Eng. Res. Inst., Kyoto Univ. Bulletin of the Engineering Research Institute, Kyoto University.
Bull. Entomological Res. Bulletin of Entomological Research. London.
Bull. Far Eastern Branch Acad. Sci. U.S.S.R. Bulletin of the Far Eastern Branch of the Academy of Sciences of the U.S.S.R.
Bull. Geol. Inst. Manchoukuo. Bulletin of the Geological Institute of Manchoukuo.
Bull. Geol. Soc. Amer. Bulletin of the Geological Society of America. New York.
Bull. Geol. Survey China. Bulletin of the Geological Survey of China. Nanking.
Bull. Govt. Res. Inst. Ceram. (Kyoto). Bulletin of Government Research Institute for Ceramics.
Bull. Histol. Appl. Path. Tech. Microscop. Bulletin d'histologie appliquée à la physiologie et à la pathologie et de technique microscopique.
Bull. Imp. Inst. Bulletin of the Imperial Institute. London.
Bull. India Sect. Electrochem. Soc. Bulletin of the Indian Section, the Electrochemical Society. Bangalore.
Bull. Inst. Agron. et Stas. Recherches Gembloux. Bulletin de l'Institut Agronomique et des Stations de Recherches de Gembloux. Gembloux, Belgium.
Bull. Inst. Chem. Res. Kyoto Univ. Bulletin of the Institute for Chemical Research, Kyoto University. Osaka, Japan.
Bull. Inst. Internat. Froid. Bulletin, Institut International du Froid. Paris.
Bull. Inst. Min. Met. Bulletin of the Institution of Mining and Metallurgy. London.
Bull. Inst. Nucl. Sci. (Belgrade). Belgrade.
Bull. Inst. Océanograph. Bulletin de l'Institut Océanographique. Monaco.
Bull. Inst. Paper Chem. Bulletin of the Institute of Paper Chemistry. Appleton, Wis.
Bull. Inst. Phys. Chem. Res. Tokyo. Bulletin of the Institute of Physical and Chemical Research. Tokyo.
Bull. Inst. Polyt. Ivanovo-Vosniesensk. Bulletin de l'Institut Polytechnique à Ivanovo-Vosniesensk.
Bull. Int. Inst. Refrig. Bulletin of the International Institute of Refrigeration. Paris.
Bull. Intern. Acad. Polonaise. Bulletin International de l'Académie Polonaise des Sciences et des Lettres. Cracow, Poland.
Bull. Intern. Acad. Polonaise, Classe Sci. Math. et Nat. Bulletin international de l'académie polonaise des sciences et des lettres. Classe des sciences mathématiques et naturelles.
Bull. Japan. Soc. Sci. Fisheries. Bulletin of the Japanese Society of Scientific Fisheries. Tokyo.
Bull. Johns Hopkins Hosp. Bulletin of the Johns Hopkins Hospital. Baltimore.
Bull. Kobayashi Inst. Phys. Res. Bulletin of the Kobayashi Institute of Physical Research.
Bull. Minnesota Univ. Eng. Expt. Stat. Engineering and Experimental Station Bulletin. University of Minnesota. Minneapolis.
Bull. Nagoya Inst. Technol. Bulletin of Nagoya Institute of Technology. Nagoya, Japan.
Bull. Naniwa Univ. Bulletin of Naniwa University.
Bull. Nat. Formulary Comm. Bulletin of the National Formulary Committee. Washington.
Bull. Nat. Res. Counc. Bulletin of the National Research Council. Washington.
Bull. Offic. Direction Rech. Sci. Ind. Inventions. Bulletin Official de la Direction des Recherches Scientifiques et Industrielles et des Inventions.
Bull. Orto Botan. Univ. Napoli. Bullettino dell'Orto Botanico della Università di Napoli. Naples.
Bull. Res. Council Israel. Bulletin of the Research Council of Israel.
Bull. Res. Inst. Food Sci. Kyoto Univ. Bulletin of the Research Institute for Food Science, Kyoto University, Osaka, Japan.
Bull. Res. Inst. Keikoku Jinzo Kenshi Kaisha Ltd. Bulletin of the Research Institute Keikoku Jinzo Kenshi Kaisha Ltd.
Bull. Rubber Growers' Assoc. Bulletin of the Rubber Growers' Association. London.
Bull. Sci. Acad. Roy. Belg. (See *Bull. Acad. Roy. Belg.*).
Bull. Sci. Pharmacol. Bulletin des Sciences Pharmacologiques. Paris.
Bull. Sect. Sci. Acad. Roum. Bulletin de la Section Scientifique de l'Academie Roumaine. Bukarest.
Bull. Sericul. Expt. Sta. Tokyo. Bulletin of the Sericulture Experiment Station, (Tokyo). Tokyo.
Bull. Soc. Chim. Bulletin de la Société Chimique de France. Paris.
Bull. Soc. Chim. Belg. Bulletin de la Société Chimique de Belgique. Brussels.
Bull. Soc. Chim. Belgrade. Bulletin de la Société Chimique Belgrade. Belgrade.
Bull. Soc. Chim. Biol. Bulletin de la Société de Chimie Biologique. Paris.

Bull. Soc. Chim. România. Bulletin de la Société chimique de România.
Bull. Soc. Chim. Roy. Yougoslav. Bulletin de la Société Chimique du royaume de Yougoslavie.
Bull. Soc. Encourag. Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Paris.
Bull. Soc. Franç. Cer. Bulletin de la Société Française de Céramique. Paris.
Bull. Soc. Franç. Elec. Bulletin de la Société Française des Electriciens. Malakoff.
Bull. Soc. Franç. Min. Bulletin de la Société Française de Minéralogie. Paris.
Bull. Soc. Franç. Min. Crist. Bulletin de la Société Française de Minéralogie et de Cristallographie. Paris.
Bull. Soc. Geol. Bulletin de la Société Géologique de France. Paris.
Bull. Soc. Ind. Min. Bulletin de la Société de l'Industrie Minérale de St. Étienne. Paris.
Bull. Soc. Industr. Mulhouse. Bulletin de la Société Industrielle de Mulhouse. Mulhouse.
Bull. Soc. Internat. Elec. Bulletin de la Société Internationale des Électriciens. Paris.
Bull. Soc. Naturalistes Moscou. Bulletin de la Société Imperiale des Naturalistes de Moscou. Moscow.
Bull. Soc. Path. Exot. Bulletin de la Société de Pathologie Exotique et de ses Filiales. Paris.
Bull. Soc. Pharm. Bordeaux. Bulletin de la Société de Pharmacie de Bordeaux.
Bull. Soc. Philomath. Bulletin de la Société Philomathique. Paris.
Bull. Soc. Phys. Bulletin de la Société Française de Physique. Paris.
Bull. Soc. Phys. Séances. Bulletin de la Société Française de Physique. Séances. Paris.
Bull. Soc. Roum. Neurol., Psychiatrie, Physiologie, Endocrinol. Bulletin de la Société Roumaine de Neurologie, Psychiatrie, Physiologie et Endocrinologie.
Bull. Soc. Roum. Phys. Bulletin de la Société Roumaine de Physique. Bukarest.
Bull. Soc. Roy. Sci. Liège. Bulletin de la Société Royale des Sciences de Liège. Liège.
Bull. Soc. Sci. Bretagne. Bulletin de la Société Scientifique de Bretagne. Rennes.
Bull. Soc. Sci. Cluj. (See *Bul. Soc. Ştiinţe Cluj*).
Bull. Soc. Sci. Hyg. Aliment. Bulletin de la Société Scientifique d'Hygiene Alimentaire et d'Alimentation Rationnelle de l'Homme. Paris.
Bull. Soc. Vaud. Sci. Nat. Bulletin de la Société Vaudoise des Sciences Naturelles. Lausanne.
Bull. State Inst. Agr. Microbiol. (U.S.S.R.). Bulletin of the State Institute of Agricultural Microbiology. Moscow.
Bull. State Inst. Marine Trop. Med. Gdansk. Bulletin of the State Institute of Marine and Tropical Medicine in Gdansk. Poland.
Bull. St. Francis Sanatorium. Bulletin of the St. Francis Hospital and Sanatorium, Roslyn, N.Y. New York.
Bull. Tech. A.I.Br. Bulletin technique A.I. Br. (Association des Ingenieurs sortis de l'Université Libre de Bruxelles).
Bull. Tech. Univ. Istanbul. Bulletin of the Technical University of Istanbul.
Bull. Tokyo Inst. Technol. Tokyo.
Bull. Tokyo Univ. Eng. Tokyo Imperial University. Faculty of Engineering. Bulletin. Tokyo.
Bull. Tokyo Univ. Forests. Bulletin of Tokyo University Forests. Tokyo.
Bull. Trav. Soc. Pharm. Bordeaux. Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
Bull. Tulane Univ. Med. Fac. Bulletin of the Tulane University Medical Faculty. New Orleans.
Bull. Univ. Illinois Eng. Expt. Station. Bulletin of the University of Illinois Engineering Experimental Station. Urbana, Ill.
Bull. U.S. Geol. Survey. Bulletins of the United States Geological Survey, Department of the Interior. Washington.
Bull. Volcanol. Bulletin Volcanologique. Naples.
Bull. Waseda Col. Eng. Bulletin of Waseda College of Engineering. Japan.
Bumazh. Prom. Bumazhnaya Promyshlennost. (Paper Industry). Moscow.
Bur. Mines Bull. Bureau of Mines Bulletin. Washington.
Bur. Mines Rep. Invest. Bureau of Mines Reports of Investigations. Washington.
Bur. Mines Tech. Paper. Bureau of Mines Technical Papers. Washington.
Bur. Stand. Bull. Bulletin of the Bureau of Standards. Washington.
Bur. Stand. Circ. Bureau of Standards Circulars. Washington.
Bur. Stand. J. Res. Journal of Research of the National Bureau of Standards. Washington.
Bur. Stand. Misc. Publ. Bureau of Standards Miscellaneous Publications. Washington.
Bur. Stand. Sci. Pap. Bureau of Standards Scientific Papers.
Byull. Eksptl. Biol. Med. Byulleten' Eksperimental'noi Biologii i Meditsiny. Moscow.
Byull. Inst. Galurgii. Byulleten' Instituta Galurgii.
Byull. IVNITI. Byulleten' IVNITI.

Byull. Nauch.-Issledovatel. Khim. Farm. Inst. (*Khimiko-Farmatsevticheskaya Promyshlennost*). Byulleten' Nauchno-Issledovatel'skovo Khimiko-Farmatsevticheskovo Instituta.
Cahiers Phys. Cahiers de Physique. Paris.
Caliche.
Calif. Dept. Nat. Resources, Spec. Rept. Californian Department of Natural Resources Special Report. San Francisco.
Calif. J. Mines Geol. California Journal of Mines and Geology. San Francisco.
Cambr. and Dublin Math. J. Cambridge and Dublin Mathematical Journal. Cambridge.
Cambr. Math. J. Cambridge Mathematical Journal. Cambridge.
Cambr. Phil. Soc. Cambridge Philosophical Society. Cambridge.
Can. J. Agr. Sci. Canadian Journal of Agricultural Science. Ottawa.
Canad. Chem. J. Canadian Chemical Journal. Toronto.
Canad. Chem. Met. Canadian Chemistry and Metallurgy. Toronto.
Canad. Chem. Process Ind. Canadian Chemistry and Process Industries. Toronto.
Canad. Chem. Prog. Canadian Chemical Progress.
Canad. Dept. Mines Tech. Surveys, Mines Branch, Topical Rept. Canadian Department of Mines and Technical Surveys, Mines Branch, Topical Report. Ottawa.
Canad. J. Chem. Canadian Journal of Chemistry. Ottawa.
Canad. J. Biochim. and Physiol. Canadian Journal of Biochemistry and Physiology. Ottawa.
Canad. J. Med. Sci. Canadian Journal of Medical Science. Ottawa.
Canad. J. Med. Technol. Canadian Journal of Medical Technology. Hamilton, Ont.
Canad. J. Phys. Canadian Journal of Physics. Ottawa.
Canad. J. Res. Canadian Journal of Research. Several Sections (A, B etc.). Ottawa.
Canad. J. Tech. Canadian Journal of Technology. Ottawa.
Canad. Med. Assoc. J. Canadian Medical Association Journal. Toronto.
Canad. Metals Met. Ind. Canadian Metals and Metallurgical Industries. Toronto.
Canad. Mining Met. Bull. Canadian Mining and Metallurgical Bulletin. Montreal.
Canad. Min. J. Canadian Mining Journal. Quebec.
Cancer Res. Cancer Research. Chicago, Cambridge.
Canner. Chicago.
Caoutchouc and Rubber U.S.S.R. Moscow.
Carnegie Inst. Publ. Carnegie Institution of Washington. Publications. Washington.
Carnegie Inst. Technol. Tech. Rep. Carnegie Institute of Technology, Technical Report.
Časopis Českoslov. Lékárnictvá. Časopis Československeho Lékárnictvá. Prague.
Časopis Lékářů Českých. Prague.
Cellulose Ind. (*Tokyo*). Cellulose Industry. Tokyo.
Cement and Lime Manuf. Cement and Lime Manufacture. London.
Centr. Bakt. Parasitenk. (See *Zent. Bakt. Parasitenk.*).
Centr. Min. Centralblatt für Mineralogie, Geologie und Paläontologie. Sect. A (Mineralogie und Petrographie). Sect. B (Geologie und Paläontologie). Stuttgart. [Section A quoted unless otherwise stated].
Centr. Natl. Recherche Sci. Groupe Franç. Argiles, Compt. Rend. Réunions Études. Centre national de la Recherche Scientifique, Group Française des Argiles, Compte rendu des Réunions d'Études. Paris.
Centr. Zuckerind. Centralblatt für die Zuckerindustrie. Magdeburg.
Ceram. Abstr. Ceramic Abstracts. Columbus.
Ceram. Age. Ceramic Age. Cleveland, Ohio.
Céram. et Verrerie. Céramique et Verrerie.
Ceram. Ind. Ceramic Industry. Chicago.
Céramique. La Céramique. Paris.
Cereal Chem. Cereal Chemistry. Minneapolis.
Ceylon Coconut Quart. Ceylon Coconut Quarterly. Lunuwila, Ceylon.
Chaleur et Ind. Chaleur et Industrie. Paris.
Chem. Age. Chemical Age. London.
Chem. Age. (*India*). Chemical Age of India. Bombay.
Chem. Age. (*N.Y.*). Chemical Age, New York.
Chem. Anal. Chemist Analyst. Phillipsburg, N.J.
Chem. App. Chemische Apparatur. Leipzig.
Chem. and Ind. Chemistry and Industry. London.
Chem. and Process Eng. Chemical and Process Engineering. London.
Chem. Ber. (See *Ber.*).
Chem. Bull. Chicago. Chemical Bulletin. Chicago.
Chem. Centr. (See *Chem. Zentr.*).

Chem. Corps J. Chemical Corps Journal. Washington.
Chem. Eng. Chemical Engineering. New York.
Chem. Eng. (Japan). Chemical Engineering (Japan). Tokyo.
Chem. Eng. Mining Rev. Chemical Engineering and Mining Review. Melbourne.
Chem. Eng. News. Chemical Engineering News. (American Chemical Society). Washington.
Chem. Eng. Prog. Chemical Engineering Progress. New York.
Chem. Eng. Prog. Symposium Ser. Chemical Engineering Progress, Symposium Series. New York.
Chem. Eng. Prog. Symposium Ser. Ultrasonics. Chemical Engineering Progress, Symposium Series. Ultrasonics. New York.
Chem. Eng. Sci. Chemical Engineering Science. New York, London.
Chem. Erde. Chemie der Erde. Jena.
Chem. Fabr. Die chemische Fabrik. Leipzig. [Formerly Part B of Zeitschrift des Vereins deutscher Chemiker].
Chem. Gazette. Chemical Gazette. London.
Chem. High Polymers (Japan). Chemistry of High Polymers. Tokyo.
Chem. Ind. Chemische Industrie (Düsseldorf).
Chem. Industries. Chemical Industries. New York.
Chem. Ing. Techn. (See *Chemie Ingenieur Technik*).
Chem. Listy. Chemické Listy pro vědu a Průmysl. Prague.
Chem. Met. Eng. Chemical and Metallurgical Engineering. New York.
Chem. News. Chemical News. London.
Chem. Obzor. Chemický Obzor. Prague.
Chem. Processing. Chemical Processing. Chicago.
Chem. Prod. Chemical Products and the Chemical News. London.
Chem. Průmysl. Chemický Průmysl. (Chemical Industry). Prague.
Chem. Rev. Chemical Reviews. Washington.
Chem. Techn. Die Chemische Technik. Leipzig.
Chem. Trade J. Chemical Trade Journal and Chemical Engineer. London.
Chem. Weekbl. Chemisch Weekblad. Hilversum.
Chem. Zentr. Chemisches Zentralblatt. Berlin.
Chem.-Ztg. Chemiker-Zeitung. Cöthen.
Chem. Zvesti. Chemické Zvesti. Bratislava.
Chemia (Buenos Aires). Buenos Aires.
Chemi. Prague.
Chemie der Erde. Jena.
Chemie Ingenieur Technik. (See *Z. Verein D. Ing., Beih. Verfahrungstechnik*).
Chemik (Gliwice). Warsaw.
Chemist & Druggist. The Chemist and Druggist. London.
Chim. Anal. Chimie Analytique. Paris.
Chim. Chronika, Greece. Chimika Chronika. Athens.
Chim. e Ind. La Chimica e l'Industria. Milan.
Chim. et Ind. Chimie et Industrie. Paris.
Chim. Ind. Agr. Biol. Chimica nell'industria, nell'agricoltura, nella biologia e nelle realizzazioni corporative.
Chimia (Switz.) Chimia (Switzerland). Aarau.
Chimica (Brazil). Chimica. São Paulo.
Chimica. Milan.
Chinese Chem. J. (See *J. Chinese Chem. Soc.*).
Chinese J. Phys. Chinese Journal of Physics. Shanghai.
Chinese J. Physiol. Chinese Journal of Physiology. Peking.
Chinese Med. J. Chinese Medical Journal. Peiping.
Chromosoma. Berlin.
Chymia. Chymia. Annual Studies in the History of Chemistry. Philadelphia.
Ciel et Terre. Ciel et Terre. Uccle, Belgium.
Ciencia, Mex. Ciencia, Mexico.
Ciencia e Invest. Ciencia e Investigacion. Buenos Aires.
Circulation. New York.
Circulation Research. New York.
Citrus Ind. Citrus Industry. Bartow, Fla.
Citrus Leaves. Los Angeles, Calif.
Civilingenieur. Der Civilingenieur. Leipzig.
Clay Minerals Bull. Clay Minerals Bulletin. Cambridge.

Cleveland Clin. Quart. Cleveland Clinic Quarterly. Cleveland.
Clin. Sci. Clinical Science incorporating Heart. Cambridge.
Coke and Chem. U.S.S.R. Koks i Khimiya. (U.S.S.R.). Moscow.
Coke Gas. Coke and Gas. London.
Cold Spring Harbor Symposia Quant. Biol. Cold Spring Harbor Symposia on Quantitative Biology. New York.
Coll. Chem. Colloid Chemistry. New York.
Coll. Czech. Chem. Comm. Collection of Czechoslovak Chemical Communications. Prague.
Coll. Guardian. The Colliery Guardian and Journal of the Iron and Coal Trades. London.
Coll. Intern. Centre Natl. Recherche Sci. (Paris). Colloques Internationaux du Centre National de la Recherche Scientifique. Paris.
Coll. Intern. Spectrographie Strasbourg. Colloque International de Spectrographie de Strasbourg. Paris.
Coll. J. U.S.S.R. Kolloid Zhurnal (Journal of Theoretical and Applied Colloid Chemistry and Physics). Moscow.
Coll. Rep. (See *B.A. Rep. Coll. Chem.*).
Coll. Res. Nat. Phys. Lab. Collected Researches. National Physical Laboratory. London.
Coll. Sympos. Ann. Colloid Symposium Annual. New York.
Colloq. Sensibilité Phot. Paris. Colloque Sensibilité Photographie. Paris.
Colon. Geol. Min. Res. Colonial Geology and Mineral Resources. London.
Comm. Fertilizer. Commercial Fertilizer. Atlanta.
Comm. Fertilizers Yearbook. Commercial Fertilizers Yearbook. Atlanta.
Comm. Kodak Res. Lab. Communications of the Kodak Research Laboratory. Rochester, New York.
Comm. Leiden. Communications from the Physical [Kamerlingh Onnes] Laboratory of the University of Leiden. Leiden.
Comment. Phys. Math. Soc. Sci. Fenn. Societas Scientiarum Fennica Commentationes Physica-Mathematicae. Helsinki.
Comment. Soc. Reg. Sci. Gottingen. Commentationes Societatis Regiae Scientiarum Gottingensis, 1778-1808, ibid., Recentiores, 1808-41. Göttingen.
Complete Abstr. Japan. Chem. Lit. Complete Abstracts of Japanese Chemical Literatures. Sandai.
Compressed Air Mag. Compressed Air Magazine. Phillipsburg.
Compt. Rend. Comptes Rendus hebdomadaires des Séances de l'Académie des Sciences. Paris.
Compt. Rend. Acad. Agr. France. Comptes Rendus des Séances del'Académie d'Agriculture de France. Paris.
Compt. Rend. Acad. Sci. Roum. Comptes Rendus des Séances de l'Académie des Sciences de Roumanie. Jassy.
Compt. Rend. Acad. Sci. U.R.S.S. Comptes Rendus (Doklady) de l'Académie des Sciences de l'U.R.S.S.
Compt. Rend. Soc. Biol. Comptes Rendus des Séances de la Société de Biologie. Paris.
Compt. Rend. Soc. Geol. Finlande. Compte rendu sommaire des séances de la société géologique de Finlande.
Compt. Rend. Soc. Phys. et Hist. Nat. Genève. Compte Rendu des Séances de la Société de Physique et d'Histoire Naturelle de Genève. Geneva.
Compt. Rend. Trav. Faculté Sci. Marseille. Comptes Rendus des Travaux de la Faculté des Sciences de Marseille. Marseille.
Compt. Rend. Trav. Lab. Carlsberg, Sér. Chim. Comptes rendus des travaux du laboratoire Carlsberg, série chimique. Copenhagen.
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Deut. Baumwollind. Deutsche Baumwollindustrie.

Deut. Färber-Ztg. Deutsche Färber-Zeitung [vereinigt mit der Leipziger Farber und Zeugdrucker-Zeitung. Liegnitz.

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Deut. Heilpflan. Deutsche Heilpflan.

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Deut. Landw. Rundschau. Deutsche Landwirtschaftliche Rundschau. Stuttgart.

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Forschungsdienst. Neudamm, Germany.
Forst. Centralblatt. Forstwissenschaftliches Centralblatt. Berlin.
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Fortschr. Landw. Fortschritte der Landwirtschaft.
Fortschr. Min. Krist. Petr. Fortschritte der Mineralogie, Kristallographie und Petrographie. Stuttgart.
Fortschr. Phys. Fortschritte der Physik. Berlin.
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Gann. Tokyo.
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Ges. Schiess-Sprengstoffw. (See *Z. ges. Schiess. u. Spreng.*).
Gesundh. Ing. Gesundheits-Ingenieur. Munich.
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Isis. Ghent.
Issledov. Priklad. Khim. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk. Issledovaniya po Prikladnoi Khimii Akademiya Nauk S.S.S.R., Otdelenie Khimicheskikh Nauk. Moscow.
Issledov. v. Oblasti Khromatog., Trudy Vsesoyuz, Soveshchaniya Khromatog., Akad. Nauk S.S.S.R., Otdel. Khim. Nauk i. Neorg. Khim.
Isvest. Fis. Nauk. Isvestiya Seriya Fisicheskaya. Moscow.
Iva. Stockholm.
Iwata Inst. Plant Biochem. Iwata Institute of Plant Biochemistry. Japan.
Izvest. Akad. Nauk Armyan. S.S.R., Ser. Fiz.-Mat. Estestven. i Tech. Nauk. Izvestiya Akademii Nauk Armyanskoi S.S.R., Fiziko-Matematicheskie, Estestvennye i Tekhnicheskie Nauki.
Izvest. Akad. Nauk Kazakh. S.S.R., No. 123, Ser. Khim. Izvestiya Akademii Nauk Kazakhskoĭ S.S.R., No. 123, Seriya Khimicheskaya.
Izvest. Akad. Nauk S.S.S.R. Izvestiya Akademii Nauk Soyuza Sovetskikh Sotsialisticheskikh Respublik.
Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk Tekh. Izvestiya Akademii Nauk S.S.S.R., Otdelenie Khimicheskikh Nauk Tekhnicheskikh. Moscow.
Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk. Izvestiya Akademii Nauk S.S.S.R., Otdelenie Tekhnicheskikh Nauk. Moscow.
Izvest. Akad. Nauk S.S.S.R., Ser. Fiz. Izvestiya Akademii Nauk S.S.S.R., Seriya Fizicheskaya. Moscow.
Izvest. Fiz.-Khim. Nauch.-Issledovatel. Inst. Irkutsk Univ. Izvestiya Fiziko-Khimicheskikh Nauchno-Issledovatel'skovo Instituta Irkutsk-Universitete. Moscow.
Izvest. Nov. Izvestiya Noveĭsheĭ Sel'sko-Khozyaĭstvennoĭ Tekhnikí.
Izvest. Polytechn. Inst. Novocherkassk. Izvestiya Polytechnicheskovo Instituta Novocherkassk. Moscow.
Izvest. Sekt. Fiz.-Khim. Anal. Akad. Nauk S.S.S.R. Izvestiya Sektora Fiziko-Khimicheskovo Analiza, Akademiya Nauk S.S.S.R. Moscow.
Izvest. Sekt. Fiz.-Khim. Anal. Inst. Obshcheĭ i Neorg. Khim. Akad. Nauk S.S.S.R. Izvestiya Sektora Fiziko-Khimicheskovo Analiza, Institut Obshcheĭ i Neorganicheskoĭ Kkimii imeni N. S. Kurnakova, Akademiya Nauk S.S.S.R. Moscow.
Izvest. Sekt. Platiny i Drug, Blagarod. Metal., Akad. Nauk S.S.S.R., Inst. Obshcheĭ i Neorg. Khim. Izvestiya Sektora Platiny i Drugykh Blagorodnykh Metallov, Institut Obshcheĭ i Neorganicheskoĭ Khimii imeni N. S. Kurnakova, Akademiya Nauk S.S.S.R. Moscow.
Izvest. Timiryazev. Sel'skokhoz. Akad. Izvestiya Timiryazevskoĭ Sel'skokhozyaistvennoĭ Akademii. Moscow.
Izvest. Tomsk. Politekh. Inst. Izvestiya Tomskovo Politekhnicheskovo Instituta. Tomsk, U.S.S.R.
Izvest. Vsesoyuz. Teplotekh. Inst. Izvestiya Vsesoyuznovo Teploteknicheskovo Instituta. (Bulletin of the Thermo-Technical Institute). Moscow.
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J.A.M.A. Journal of the American Medical Association. Chicago.
J. Acoust. Soc. Amer. Journal of the Acoustical Society of America. New York.
J. Agr. Chem. Soc. Japan. Journal of the Agricultural Chemical Society of Japan. Tokyo.
J. Agr. Food Chem. Journal of Agricultural and Food Chemistry. Washington.
J. Agr. Prat. Journal d'Agriculture Pratique et Journal de l'Agriculture. Paris.
J. Agr. Res. Journal of Agricultural Research. Washington.
J. Agr. Sci. Journal of Agricultural Science. Cambridge.
J. Amer. Ceram. Soc. Journal of the American Ceramic Society. Columbus, Ohio.
J. Amer. Concrete Inst. Journal of the American Concrete Institute. Shepherdsville, Ky.
J. Amer. Dental Assoc. Journal of the American Dental Association. Chicago.
J. Amer. Dietet. Assoc. Journal of the American Dietetic Association. Chicago.
J. Amer. Inst. Elec. Eng. Journal of the American Institute of Electrical Engineers. New York.
J. Amer. Leather Chem. Journal of the American Leather Chemists' Association. Cincinnati.
J. Amer. Med. Assoc. Journal of the American Medical Association. Chicago.
J. Amer. Oil Chemists' Soc. Journal of the American Oil Chemists' Society. Chicago.

J. Amer. Orient Soc. Journal of the American Oriental Society. New York.
J. Amer. Pharm. Assoc. Journal of the American Pharmaceutical Association. Washington.
J. Amer. Rocket Soc. Journal of the American Rocket Society. New York.
J. Amer. Soc. Agron. Journal of the American Society of Agronomy. Madison, Wis.
J. Amer. Soc. Mech. Eng. Journal of the American Society of Mechanical Engineers. New York.
J. Amer. Soc. Refrig. Eng. Journal of the American Society of Refrigerating Engineers. New York.
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J. and Proc. Indian Chem. Soc. Journal and Proceedings of the Indian Chemical Society. Calcutta.
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J. Antibiotics (Japan). Journal of Antibiotics (Japan). Tokyo.
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J. Appl. Chem. U.S.S.R. Journal of Applied Chemistry U.S.S.R.
J. Appl. Mechan. Journal of Applied Mechanics. Issued as part of the Transactions of the American Society of Mechanical Engineers. New York.
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J. Appl. Phys. U.S.S.R. Journal of Applied Physics. Moscow.
J. Appl. Physiol. Journal of Applied Physiology. Washington.
J. Asiat. Journal Asiatique. Paris.
J. Assoc. Offic. Agr. Chem. Journal of the Association of Official Agricultural Chemists. Washington.
J. Atmospheric Terrest. Phys. Journal of Atmospheric and Terrestrial Physics. London.
J. Australian Inst. Agr. Sci. Journal of the Australian Institute of Agricultural Science Melbourne.
J. Australian Inst. Met. Journal of the Australian Institute of Metals. Victoria.
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J. Bath West and Southern Counties Soc. Encour. Agr. Journal of the Bath and West and Southern Counties Society for the Encouragement of Agriculture, Arts, Manufactures and Commerce. Bath.
J. Biochem. (Japan). Journal of Biochemistry (Japan). Tokyo.
J. Biol. Chem. Journal of Biological Chemistry. Baltimore.
J. Birmingham Met. Soc. Journal of the Birmingham Metallurgical Society. Birmingham.
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J. Chem. Soc. Japan. Journal of the Chemical Society of Japan. Tokyo.
J. Chem. Soc. Muslim Univ. Aligarh. Journal of the Muslim University Chemical Society. Aligarh.
J. Chim. Phys. Journal de Chimie Physique. Geneva, and (from 1906) Paris.
J. China Soc. Chem. Ind. Journal of the China Society of Chemical Industry.
J. Chinese Chem. Soc. Journal of the Chinese Chemical Society. Peiping.
J. Chosen Med. Assoc. Journal of the Chosen Medical Association.
J. Clin. Endocrinol. The Journal of Clinical Endocrinology. Springfield, Ill.
J. Clin. Endocrin. and Metabolism. Journal of Clinical Endocrinology and Metabolism. Springfield, Ill.
J. Clin. Invest. The Journal of Clinical Investigation. New Haven, Conn.

J. Coal Res. Inst. (*Japan*). Journal of the Coal Research Institute, Japan. Tokyo.

J. Coll. Sci. Imp. Univ. Japan. Journal of the College of Science. Imperial University of Tokyo. Tokyo.

J. Colloid Sci. Journal of Colloid Science. New York.

J. Colo.-Wyo. Acad. Sci. Journal of the Colorado/Wyoming Academy of Science. Denver, Colo.

J. Comm. N.Y. Journal of Communications. New York.

J. Conseil Intern. Exploration Mer. Journal du Conseil, Conseil Permanent International pour l'Exploration de la Mer. Copenhagen.

J. Counc. Sci. Ind. Res. (*Australia*). Journal of the Council for Scientific and Industrial Research. Melbourne.

J. Dairy Res. Journal of Dairy Research. Cambridge.

J. Dairy Sci. Journal of Dairy Science. Champaign, Ill.

J. de l'École Polytechn. Journal de l'École Polytechnique. Paris.

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J. de Phys. Journal de Physique Théorique et Appliquée. Paris.

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J. Electrochem. Assoc. Japan. Journal of the Electrochemical Association of Japan. Tokyo.

J. Electrochem. Soc. Journal of the Electrochemical Society. New York.

J. Electrochem. Soc. Japan. Journal of the Electrochemical Society, Japan. Tokyo.

J. Electrodepos. Techn. Soc. Journal of the Electrodepositors' Technical Society. London.

J. Electropl. Depos. Techn. Soc. Journal of the Electroplaters' and Depositors' Technical Society. London.

J. Elisha Mitchell Sci. Soc. Journal of the Elisha Mitchell Scientific Society. North Carolina University, Chapel Hill, N.C.

J. Exptl. Biol. Journal of Experimental Biology. Cambridge.

J. Exptl. Botany. Journal of Experimental Botany. Oxford.

J. Exptl. Med. Journal of Experimental Medicine. Baltimore, New York.

J. Exptl. Theor. Phys. U.S.S.R. Journal of Experimental and Theoretical Physics U.S.S.R. Moscow, Leningrad.

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J. Fac. Agr., Kyushu Univ. Journal of the Faculty of Agriculture, Kyushu University. Fukuoka, Japan.

J. Fac. Eng. Tokyo. Imperial University, Tokyo. Journal of the Faculty of Engineering. Tokyo.

J. Fac. Sci. Imp. Univ. Tokyo. Imperial University, Tokyo. Journal of the Faculty of Science. Tokyo.

J. Fermentation Assoc. Japan. Journal of the Fermentation Association of Japan. Tokyo.

J. Fermentation Technol. (*Japan*). Journal of the Fermentation Technology. (*Hakkô Kôgaku Zasshi*). Osaka.

J. Fisheries Board Can. Journal of the Fisheries Research Board of Canada. Ottawa.

J. Forestry. Journal of Forestry. Washington.

J. Four Elec. Journal du Four Electrique. Paris.

J. Franklin Inst. Journal of the Franklin Institute. Philadelphia.

J. Fuel Soc. Japan. Journal of the Fuel Society of Japan. Tokyo.

J. Gasbeleucht. Journal für Gasbeleuchtung. Munich.

J. Gas Lighting. Journal of Gas Lighting and Water Supply. London.

J. Gen. Chem. U.S.S.R. Journal of General Chemistry U.S.S.R. Moscow.

J. Gen. Physiol. Journal of General Physiology. New York.

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J. Geol. Acad. Sci. Ukrain. S.S.R. Journal of Geology, Ukrainian Academy of Sciences. S.S.R.

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J. Gerontol. Journal of Gerontology. St. Louis, Mo.

J. Histochem. and Cytochem. Journal of Histochemistry and Cytochemistry. Baltimore, Madison.

J. Hotel-Dieu Montreal. Journal de l'Hotel-Dieu de Montreal. Montreal.

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J. Hyg. Journal of Hygiene. Cambridge.
J. Immunol. Journal of Immunology. Baltimore.
J. Imp. Coll. Chem. Eng. Soc. Journal of the Imperial College Chemical Engineering Society. London.
J. Ind. Eng. Chem. Journal of Industrial and Engineering Chemistry. Washington.
J. Ind. Explosives Soc. Japan. Journal of the Industrial Explosives Society. Tokyo.
J. Ind. Hyg. Toxicol. Journal of Industrial Hygiene and Toxicology, with Abstract of the Literature. Baltimore.
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J. Indian Chem. Soc. Journal of the Indian Chemical Society. Calcutta.
J. Indian Inst. Sci. Journal of the Indian Institute of Science. Bangalore.
J. Indian Soc. Soil Sci. New Delhi.
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J. Inorg. Nucl. Chem. Journal of Inorganic and Nuclear Chemistry. London.
J. Inst. Chem. Journal of the Institute of Chemistry (now Journal of the Royal Institute of Chemistry). London.
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J. Inst. Elec. Engrs. Japan. Journal of the Institute of Electrical Engineers. Tokyo.
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J. Inst. Heating and Ventilating Eng. Journal of the Institute of Heating and Ventilating Engineers. London.
J. Inst. Met. Journal of the Institute of Metals and Metallurgical Abstracts. London.
J. Inst. Petrol. Journal of the Institute of Petroleum. London.
J. Inst. Petrol. Techn. Journal of the Institution of Petroleum Technologists. London.
J. Inst. Polytech. Osaka City Univ. Journal of the Institute of Polytechnics, Osaka City University. Osaka.
J. Inst. Sanit. Engrs. Journal of the Institution of Sanitary Engineers. London.
J. Inst. Water Engrs. Journal of the Institution of Water Engineers. London.
J. Instr. Soc. Amer. Journal of the Instrument Society of America. Pittsburgh, Pa.
J. Internat. Soc. Leather Trades Chem. Journal of the International Society of Leather Trades' Chemists. Widnes.
J. Investigative Dermatol. Journal of Investigative Dermatology. Baltimore, Md.
J. Iron Steel Inst. Journal of the Iron and Steel Institute. London.
J. Japan. Biochem. Soc. Journal of the Japanese Biochemical Society. Tokyo.
J. Japan. Ceram. Assoc. Journal of the Japanese Ceramic Association. Tokyo.
J. Japan. Chem. Journal of Japanese Chemistry. Tokyo.
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J. Japan. Tech. Assoc. Pulp Paper Ind. Journal of the Japanese Technical Association of the Pulp and Paper Industry. Tokyo.
J. Lab. Clin. Med. Journal of Laboratory and Clinical Medicine. St. Louis.
J.-Lancet. Journal-Lancet. Minneapolis.
J. Landwirtsch. Journal für Landwirtschaft. Berlin.
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J. Marine Res. Journal of Marine Research. New Haven, Conn.
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J. Méd. Bordeaux et Sud-Ouest. Journal de Médecine de Bordeaux et du Sud-Ouest. Bordeaux.
J. Met. Ceram. Journal of Metallurgy and Ceramics.
J. Metals. Journal of Metals. New York.
J. Meteorol. Journal of Meteorology. Boston, Mass.
J. Milk Food Technol. Journal of Milk and Food Technology. New York.
J. Milk Trade Tech. Journal of Milk Trade Technology.
J. Mines. Journal des Mines. Paris.
J. Mining Inst. Japan. Journal of the Mining Institute of Japan. Tokyo.
J. Ministry Agr. Journal of the Ministry of Agriculture. London.
J. Mt. Sinai Hosp., N.Y. Journal of the Mount Sinai Hospital, New York.
J. Mysore Univ. The Half-Yearly Journal of the Mysore University. Bangalore.
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J. Nat. Cancer Inst. Journal of the National Cancer Institute. Washington.
J. Nat. Med. Assoc. Journal of the National Medical Association. New York.

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J. New England Water Works Assoc. Journal of the New England Water Works Association. Boston, Mass.
J. Nucl. Energy. Journal of Nuclear Energy. London.
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J. Org. Chem. Journal of Organic Chemistry. Washington.
J. Oriental Med. Journal of Oriental Medicine (later Manshu Igaku Zasshi), Mukden.
J. Osaka City Med. Center. Journal of the Osaka City Medical Center. Osaka.
J. Osmania Univ. Journal of the Osmania University. Hyderabad, Deccan.
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J. Penna. Water Works Operators' Assoc. Journal of the Pennsylvania Water Works Operators' Association. Bethlehem, Pa.
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J. Pharm. Chim. Journal de Pharmacie et de Chimie. Paris.
J. Pharm. Soc. Japan. Journal of the Pharmaceutical Society of Japan. Tokyo.
J. Pharmacol. Journal of Pharmacology. London.
J. Pharmacol. Exptl. Therap. Journal of Pharmacology and Experimental Therapeutics. Baltimore.
J. Phys. Journal de Physique, Théorique et Appliquée. Paris.
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J. Phys. Soc. Japan. Journal of the Physical Society of Japan. Tokyo.
J. Phys. U.S.S.R. Journal of Physics U.S.S.R. Moscow, New York.
J. Physiol. Journal of Physiology. Cambridge.
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J. Rech. Centre Nat. Journal des Recherches du Centre National de la Recherche Scientifique. Paris.
J. Reine Angew. Math. (Crelle). Journal für die reine und angewandte Mathematik (Crelle's Journal). Berlin.
J. Res. Inst. Cat., Hokkaido Univ. Journal, Research Institute for Catalysis, Hokkaido University. Japan.
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J. Roy. Army Med. Corps. Journal of the Royal Army Medical Corps. London.
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J. Roy. Soc. Arts. Journal of the Royal Society of Arts. London.
J. Roy. Soc. N.S Wales. Journal of the Royal Society of New South Wales. Sydney.
J. Roy. Techn. Coll. Glasgow. Journal of the Royal Technical College. Glasgow.
J. Rubber Res. Journal of Rubber Research. London.

J. Russ. Phys. Chem. Soc. Journal of the Russian Physical-Chemical Society. Moscow. (C = Chemistry Section, P = Physics Section).
J. S. African Chem. Inst. Journal of the South African Chemical Institute. Cape Town.
J. S. African Inst. Eng. Journal of the South African Institute of Engineers. Johannesburg.
J.S.C.I. Journal of the Society of Chemical Industry. London.
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J. Sci. and Technol. Journal of Science and Technology (India).
J. Sci. Assoc. Maharajah's College, Vizianagram. Journal of the Science Association, Maharajah's College, Vizianagram.
J. Sci. Food Agr. Journal of the Science of Food and Agriculture. London.
J. Sci. Hiroshima Univ. Journal of Science of the Hiroshima University. Hiroshima.
J. Sci. Ind. Res. India. Journal of Scientific and Industrial Research. New Delhi.
J. Sci. Instr. Journal of Scientific Instruments and of Physics in Industry. London.
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J. Sci. Soil Manure. Journal of the Science of Soil and Manure. Tokyo.
J. Sediment. Petrol. Journal of Sedimentary Petrology. Tulsa, Oklahoma.
J. Soc. Arts. (See *J. Roy. Soc. Arts*).
J. Soc. Chem. Ind. Japan. Journal of the Society of Chemical Industry. Tokyo.
J. Soc. Cosmetic Chem. Journal of the Society of Cosmetic Chemists. London.
J. Soc. Dyers Colourists. Journal of the Society of Dyers and Colourists. Bradford.
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J. Soc. Trop. Agr., Taihoku Imp. Univ. Journal of the Society of Tropical Agriculture, Taihoku Imperial University.
J. Soil Sci. Journal of Soil Science. Oxford.
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J. Tech. Phys. U.S.S.R. Journal of Technical Physics U.S.S.R. Leningrad.
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J. Urol. Journal of Urology. Baltimore, Md.
J. Usines Gaz. Journal des Usines à Gaz. Paris.
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J. Wash. Acad. Journal of the Washington Academy of Sciences. Washington.
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Jahrb. Geol. Reichsanst. Wien. Jahrbuch der Kaiserlich-Königlichen Geologischen Reichsanstalt. Vienna.
Jahrb. Hallesches Verband. Erforsch. Mitteldeut. Bodenschätze. Hallesches Jahrbuch für Mitteldeutsche Erdgeschichte. Halle, Germany.
Jahrb. Hamburg. Wiss. Anst. Jahrbuch der Hamburgischen wissenschaften Anstalten, Hamburg.
Jahrb. Kinderheilk. Jahrbuch für Kinderheilkunde. Basel.
Jahrb. Min. Jahrbuch für Mineralogie, Geognosie, Geologie und Petrifaktenkunde. Heidelberg. 3 vols., 1830-2.
Jahrb. Niedersächs. Geol. Verein. Jahresbericht der Niedersächsischen Geologischen Vereins. Hanover.
Jahrb. Preuss. Geol. Landesanstalt. Jahrbuch der Preussischen Geologischen Landesanstalt. Berlin.
Jahrb. Radioakt. Elektronik. Jahrbuch der Radioaktivität und Elektronik. Leipzig.
Jahrb. Wiss. Botan. Jahrbücher für Wissenschaftliche Botanik. Germany.

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Jahres-Ber. Jahres-Bericht über die Fortschritte der Chemie und Mineralogie. Tübingen.

Jahresber. Chem. Tech. Reichsanstalt. Jahresbericht für Chemische-Technologische Reichsanstalt.

Jahresber. Limnol. Flussta Freudenthal. Jahresbericht Limnologie Flussta Freudenthal.

Jahresheft Geol. Abt., Württemberg Statist. Landesamtes. Jahresheft Geol. Abteilung, Württemberg Statistisches Landesamtes.

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Japan. J. Astron. Geophys. Japanese Journal of Astronomy and Geophysics. Tokyo.

Japan. J. Chem. Japanese Journal of Chemistry. Tokyo.

Japan. J. Med. Sci. Japanese Journal of Medical Sciences. Tokyo.

Japan. J. Phys. Japanese Journal of Physics. Tokyo.

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Johns Hopkins Univ. Johns Hopkins University Contribution. Baltimore.

K. Akad. Wetenschappen, Amsterdam. Proc. Koninklijke Nederlandse Akademie van Wetenschappen, Amsterdam. Proceedings.

K. Dansk. Videns. Selsk. Meddel. Det Kongelige Danske Videnskabernes Selskab, Matematisk-Fysiske Meddelelser. Copenhagen.

K. Norsk. Vidensk. Selsk. Forhl. Kongelige Norske Videnskabernes Selskabs Forhandlinger. Trondheim.

K. Svensk. Akad. Handl. Kongliga Svenska Vetenskaps-Akademiens Handlinger. Uppsala and Stockholm.

Kagaku (Kyoto). (Science) Kyoto.

Kagaku no Ryoîki. Tokyo.

Kali. Berlin.

Kali u. Steinsalz. Kali und Steinsalz. Essen.

Kaliĭ U.S.S.R. Moscow.

Kälte. Hamburg.

Kälteind. Kälteindustrie. Hamburg and Altona.

Kansas Expt. Sta. Tech. Bull. Kansas Agricultural Experiment Station. Kansas State University. Kansas.

Kastners Archiv. Archiv für die gesamte Naturlehre. Nürnberg, 18 vols., 1824-9.

Kautschuk. Berlin and Düsseldorf.

Keemia Teated. Bratislava.

Keijo J. Med. Keijo Journal of Medicine. Tokyo.

Kem. i Ind. (Zagreb). Kemija i Industriya Zagreb.

Kém. Lapja. Kémikusok Lapja. Budapest.

Kem. Zbornik. Kemijski Zbornik. Lubljana.

Keram. Rundschau. Keramische Rundschau. Koslar.

Keramos. Bamberg.

Kgl. Dansk. Videns. Det Kongelige Danske Videnskabernes Selskab. Skrifter. Naturvidenskabelige og Matematiske Afdeling. Copenhagen.

Kgl. Dansk. Videns. Selskab. Biol. Medd. Det Kongelige Danske Videnskabernes Selskab, Biologiske Meddelelser. Copenhagen.

Kgl. Dansk. Videns. Selskab Mat. Fys. Medd. Det Kongelige Danske Videnskabernes Selskab, Matematisk-Fysike Meddelelser. Copenhagen.

Kgl. Lantbrucks-Akad. Handl. Tid. Kungliga Lantbrucks-Akademiens Handlingar och Tidskrift. Copenhagen.

Kgl. Lantbrucks-Högskol. Ann. Kungliga Lantbrucks-Höskolans Annalen. Uppsala.

Kgl. Norske Videns. Kongelige Norske Videnskabers Selskab, Forhandlinger. Trondheim.

Khim. Farm. Prom. Khimiko-Farmatsevticheskaya Promyshlennost.

Khim. i Ind. Khimiya i Industriya. Sofia.

Khim. Mashinostroenie. Khimicheskoe Mashinostroenie. Moscow.

Khim. Prom. Khimicheskaya Promyshlennost. Moscow.

Khim. Redkikh Elementov, Akad. Nauk S.S.S.R., Inst. Obshcheĭ i Neorg. Khim. Khimiya Redkikh Elementov, Akademiya Nauk S.S.S.R., Institut Obshcheĭ i Neorganicheskoĭ Khimiĭ. Moscow.

Khim. Referat. Zhur. Khimicheskiĭ Referativnyĭ Zhurnal.

Khim. Tverdogo Topliva. Khimiya Tverdovo Topliva. Moscow.

Khimstroĭ. Moscow.

Khlopchatobumazh. Prom. Khlopchatobumazhnaya Promyshlennost. Moscow.

Kholodil'naya Prom. Kholodil'naya Promyshlennost. Moscow.

Kholodil'naya Tekh. Kholodil'naya Tekhnika. Moscow.

Kim. Inst. Zinātnisk. Raksti, Latvijas P.S.R. Zinātnu Akad. Kimijas Instituta Zinātniskie Raksti, Latvijas P.S.R. Zinātnu Akademija.

Kinzoku. (Metals). Tokyo.

Klassiker. (See *Ostwald*).

Klein. Veröffentl. Kgl. Ungar. Reichsanst. Meteor. Erdmagnet. Kleinere Veröffentlichungen der dem Kgl. Ungar. Ministerium für Ackerbau unterstehenden Reichsanstalt für Meteorologie und Erdmagnetismus. Budapest.

Kleine Mitl. Ver. Wasser. Boden. Lufthyg. Kleine Mitteilungen für die Mitglieder des Vereins für Wasser-, Boden- und Lufthygiene. Berlin-Dahlem.

Klin. Med. U.S.S.R. Klinicheskaya Meditsina (U.S.S.R.). Moscow.

Klin. Wochschr. Klinische Wochenschrift. Berlin.

Kogyo Kayaku Kyokai-Shi. Journal of the Industrial Explosives Society of Japan. Tokyo.

Koll. Beih. Kolloidchemische Beihefte. Dresden.

Koll. Z. Kolloid Zeitschrift. Darmstadt.

Koll. Zhur. Kolloidnyĭ Zhurnal. Moscow.

Kong. Veterin. Landsbohøjskole, Aarskr. Kongelige Veterinaerog Landbohøjskole, Arskrift. Copenhagen.

Koninkl. Nederland. Akad. Wetenschap., Proc. Koninklijke Nederlandse Akademie van Wetenschappen, Proceedings.

Korrosion. Weinheim.

Korrosion u. Metallschutz. Korrosion und Metallschutz. Weinheim.

Korroziya i Borba. Korroziya i Borba s Neĭ.

Korroziya i Metallopokritiya (Corrosion & Protection of Metals). Moscow.

Kosmos. Lvov.

Kranke Pflanze. Dresden.

Kumamoto Med. J. Kumamoto Medical Journal. Kumamoto, Japan.

Kunstdünger u. Leim. Kunstdünger und Leim.

Kunstseide. Die Kunstseide. Frankfurt a.M.

Kunststoffe. Munich.

Kyushu Mem. Med. Sci. Kyushu Memoirs of Medical Science. Fukuoka, Japan.

La Ceramica. Milan.

La Nature. Paris.

Lab. Allgem. Phys. Tech. Chem. (*Univ. Fernen Osterr.*). Laboratorium für Allgemeine Physikalische und Technische Chemie (Universität Fernen Österreiche).

Laboratorio. Granada.

Lancet. London.

Landbouw. Djakarta. Indonesia.

Landbouwkund. Tidschr. Landbouwkundig Tidschrift. The Hague.

Landolt-Börnstein 'Tabellen'. Landolt-Börnstein, Physikalisch-Chemische Tabellen, and Ergänzungsbände. Berlin.

Landw. Jahrb. Landwirtschaftliche Jahrbücher. Berlin.

Landw. Jahrb. für Bayern. Landwirtschaftliches Jahrbuch für Bayern.

Landw. Jahrb. Schweiz. Landwirtschaftliches Jahrbuch der Schweiz. Bern.

Landw. Vers. Sta. Landwirtschaftlichen Versuchs-Stationen

Landwirtsch. Forsch. Landwirtschaftliche Forschung. Frankfurt a.M.

Laryngoscope. St. Louis, Missouri.

Latvijas PSR Zinatnu Akad. Vestis. Latvijas PSR Zinatnu Akademijas Vestis. Riga, U.S.S.R.

Le Radium. Paris.

Le Vide. Paris.

Leather and Shoes. Chicago.

Leather Manuf. Boston, Mass.

Ledertech. Rundschau. Ledertechnische Rundschau. Berlin.

Legkaya Prom. Legkaya Promyshlennost (Light Industry). Moscow.

Legkie Metal. Legkie Metally (Light Metals). Moscow.

Leipzig Ber. Berichte über die Verhandlungen der Königlich-Sächsischen Akademie der Wissenschaften zu Leipzig. Mathematisch-Physikalische Klasse. Leipzig.

Leipzig. Monat. Text. Ind. Leipziger Monatsschrift für Textil-Industrie. Leipzig.

Leipziger Vorträge Quantentheorie Chemie. Leipziger Vorträge für Quantentheorie Chemie.

Len i Konoplya. U.S.S.R.

Licht u. Lampe. Licht und Lampe. Berlin.

Lick Observatory Bull. Lick Observatory Bulletins. Berkeley, Calif.

Liebigs Ann. Liebig's Annalen für Chemie. (See *Annalen*).

Light Metal Age. Chicago.

Light Metals. London.

L'Industria Chimica. Milan.

L'Industrie Chim. L'Industrie Chimique. Paris.

Lingnan Sci. J. Lingnan Science Journal. Lingnan University. Canton, China.

L'Institut. Paris.

Listy Cukrovar. Listy Cukrovarniké. Prague.

Lnopenkodsnutovaya Prom. Lnopenkodsnutovaya Promyshlennost.

Louisiana Planter. U.S.A.

Lunds Fys. Sällsk. Jubelskrift. Kungl. Fysiografiska Sällskapets i Lund. Jubelskrift. Lund, 1878.

Lychnos. Uppsala.

Lymphatologia Kyoto. Lymphatologia (Kyoto). Kyoto, Japan.

Maataloustieteellinen Aikakauskirja. Helsinki.

Maden Tetkik Arama. Maden Tetkik ve Arama Enstitusu Mecmuasi. Ankara.

Madras Agr. J. Madras Agricultural Journal. Coimbatore, S. India.

Mag. Kém. Lapja. Magyar Kémikusok Lapja. Budapest.

Magyar Biol. Kutatóintézet Munkái. Magyar Biológiai Kutatóintézet Munkái. Budapest.

Magyar Gyógy. Társa. Értes. Magyar Gyógyszerésztudományi Társaság Értesitője. Budapest.

Magyar Kém. Folyóirat. Magyar Kémiai Folyóirat. Budapest.

Magyar Orvosi Arch. Magyar Orvosi Archivum. Budapest.

Makromol. Chem. Die Makromolekulare Chemie. Basel.

Malayan Agr. J. Malayan Agricultural Journal. Kuala Lumpur.

Manch. Mem. Memoirs and Proceedings of the Manchester Literary and Philosophical Society. Manchester.

Manitoba Dept. Mines and Nat. Resources, Mines Branch Publ. Manitoba Department of Mines and Natural Resources, Mines Branch Publications. Winnipeg.

Marburg Ber. Sitzungsberichte der Gesellschaft zur Beförderung der gesamten Naturwissenschaften zu Marburg. Marburg.

Masloboïno-Zhirovaya Prom. Masloboïno-Zhirovaya Promyshlennost. Moscow.

Masloboïno Zhirovoe Delo. (See *Masloboïno-Zhirovaya Prom*).

Mass. Inst. Tech. Res. Lab. Electronics Tech. Rep. Massachusetts Institute of Technology, Research Laboratory of Electronics and Lincoln Laboratory Technical Report. Cambridge, Mass.

Mass. Inst. Technol. Rept. K. 729. Massachusetts Institute of Technology, Report K. 729. Cambridge, Mass.

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Materialy Nauch. Issle. Materialy Tsentral'novo Nauchno-Issledovatel'skovo Instituta po Tekstil'noĭ Promyshlennosti 'Niti'. Moscow.

Matériaux Géol. Générales Appliqués, Leningrad. Matériaux Géologiques Générales et Appliqués. Leningrad.

Materie Plastiche. Milan.

Math. Ann. Mathematische Annalen. Leipzig.

Math. Anz. Ungar. Akad. Wiss. Matematikai és Természettudomanyi Értesitö a Magyar Tudományos Akademia. Budapest.

Math. Nat. Ber. Ungarn. Mathematische und Naturwissenschaftliche Berichte aus Ungarn. Leipzig.

Math. Z. Mathematische Zeitschrift. Brunswick.

Mazda Kenkyu Jiho. Japan.

Mécanique. Paris.

Mech. Eng. Mechanical Engineering. Easton, Pa.

Mech. Eng. N.Y. Mechanical Engineering. New York.

Mechanics Magazine. London (1823-72).

Med. Doświadczalna i Mikrobiol. Medycyna Doświadczalna i Mikrobiologia. Warsaw.

Med. J. Australia. Medical Journal of Australia. Sydney.

Med. Klin. (Munich). Medizinische Klinik (Munich). Munich.

Med. Lavoro. Medicina del Lavoro, Milan.

Med. Sper. Medicina Sperimentale. Turin.

Medd. Centralanstalt Försöksväsendet Jordbruk. Meddelande från Centralanstalten för Försöksväsendert på Jordbruksområde. Malmö.

Medd. Lunds Geol.-Mineral. Inst. Meddelanden från Lunds Geologisk-Mineralogiska Institution. Lund.

Medd. Skogsförsöksanst. Stockholm.

Medd. Stat. Växtskyddum. Meddelanden från Statens Växtskyddum. Stockholm.

Meddel. Nobelinst. Meddelanden från K. Svenska Vetenskapsakademiens Nobelinstitut. Uppsala.

Medel. Landbouwhogeschool Opzoekingsstas. Staat Gent. Mededelingen van de Landbouwhogeschool en de Opzoekingsstations van de Staat te Gent. Ghent.

Medel. Vlaam. Chem. Ber. Mededelingen van de Vlaamse Chemische Vereniging. Willebrock. Belgium.

Medicine. Baltimore, Madison.

Meldinger Norg. Landbrukshøgskole. Meldinger fra Norges Landbrukshøgskole. Goevik, Norway.

Melliand Textilber. Melliand Textilberichte. Heidelberg.

Melliand Textile Monthly. New York.

Mém. Acad. Berlin. Mémoires de l'Académie Royale des Sciences et Belles-Lettres. Berlin (1786-1804).

Mem. Acad. Ciencias Arts Barcelona. Memòrias de l'Acadèmia de Ciències i Arts de Barcelona. Barcelona.

Mém. Acad. Roy. Belg. Académie Royale de Belgique. Mémoires. Classe des Sciences. Brussels.

Mém. Acad. Sci. Mémoires de l'Académie des Sciences. Paris. Abstracts of the memoirs are added to many of the volumes with the title Histoire.

Mém. Acad. St. Petersb. Mémoires de l'Académie Imperiale des Sciences de St. Petersbourg. St. Petersburg.

Mém. Acad. Turin. Mémoires de l'Académie Royale des Sciences à Turin. Turin.

Mem. Accad. Ital. Chim. Memorie della Reale Accademia d'Italia; Chimica. Rome.

Mem. Accad. Lincei. Memorie della Reale Accademia Nazionale dei Lincei. Classe di Scienze Fisiche. Rome.

Mém. Artillerie Franç. Mémorial de l'Artillerie Française. Paris.

Mém. Assoc. Ing. Ecole Liège. Mémoires de l'Association Ingénieure, Ecole Liège.

Mem. Assoc. Tecnicos Azucar. Cuba. Memoria de la Asociacion de Tecnicos Azucareros de Cuba.

Mem. Chem. Soc. Memoirs of the Chemical Society. London.

Mem. Coll. Eng. Kyushu Imp. Univ. Memoirs of the College of Engineering. Kyushu Imperial University. Fukuoka, Japan.

Mem. Coll. Sci. Kyoto Imp. Univ. Memoirs of the College of Science. Kyoto Imperial University. Kyoto.

Mém. Couronn. Acad. Roy. Belg. Mémoires Couronnés par l'Académie Royale des Sciences et Belles-Lettres de Bruxelles. Brussels.

Mém. Couronn. et Autres Acad. Roy. Belg. Mémoires Couronnés et Autres Mémoires Publiés par l'Académie Royale des Sciences, des Lettres et des Beaux-Arts de Belgique. Brussels.

Mém. Couronn. et de Sav. Étrang. Acad. Roy. Bruxelles. Mémoires Couronnés et Mémoires des Savants Étrangers, Publiés par l'Académie Royale des Sciences et Belles-Lettres de Bruxelles. Brussels.

Mem. Dept. Agr. India, Chem. Ser. Memoirs of the Department of Agriculture in India. Delhi.

Mém. Div. Sav. Acad. Sci. Mémoires Présentés par Divers Savants à l'Académie des Sciences de l'Institut de France. Paris.

Mém. Divers Sav. St. Petersbourg Acad. Mémoirs Présentés a l'Académie Impériale des Sciences de St. Petersbourg par Divers Savants et lus dans ses Assemblées. St. Petersbourg (1831-59).

Mem. Fac. Eng. Kyoto Univ. Memoirs of the Faculty of Engineering Kyoto University. Kyoto. Japan.

Mem. Fac. Eng. Kyushu Univ. Memoirs of the Faculty of Engineering Kyushu University. Fukuoka, Japan.

Mem. Fac. Sci., Kyushu Univ. Memoirs of the Faculty of Science, Kyushu University. Fukuoka, Japan.

Mem. Geol. Surv. Memoirs of the Geological Survey.

Mem. Inst. Chem. Acad. Sci. Ukr.S.S.R. Memoirs of the Intitute for Chemistry, Academy of Science of the Ukrainian S.S.R.

Mem. Inst. Sci. Ind. Res. Osaka Univ. Memoirs of the Institute of Scientific and Industrial Research, Osaka University. Osaka, Japan.

Mem. Ist. Lombard. Memorie, Reale Istituto Lombardo di Scienze e Lettere. Milan.

Mém. Mus. Hist. Nat. Mémoires du Muséum d'Histoire Naturelle. Paris.
Mém. Poudres. Mémorial des Poudres et Salpêtres. Paris.
Mem. Proc. Chem. Soc. Memoirs and Proceedings. The Chemical Society. London.
Mem. Proc. Manchester Lit. and Phil. Soc. Memoirs and Proceedings of the Manchester Literary and Philosophical Society. Manchester.
Mem. R. Accad. Torino. Memorie della Reale Accademia de Scienza di Torino. Turin.
Mem. Rev. Soc. Cien. Memorias y Revista de la Sociedad Cientifica Antonio Alzate. Mexico.
Mem. Ryojun Coll. Eng. Memoirs of the Ryojun College of Engineering. Ryojun, S. Manchuria.
Mém. Services Chim. État, Paris. Mémorial des Services Chimiques de l'État. Paris.
Mém. Soc. Arceuil. Mémoires de Physique et de Chimie de la Société d'Arceuil. Paris.
Mém. Soc. Imp. Nat. Moscou. Mémoires de la Société Imperiale des Naturalistes de Moscou. Moscow.
Mém. Soc. Lille. Mémoires de la Société Royale des Sciences, de l'Agriculture et des Arts, de Lille. Lille.
Mém. Soc. Phys. Nat. (*Geneva*). Mémoires de la Société de Physique et d'Histoire Naturelle de Genève. Geneva.
Mém. Soc. Roy. Sci. Liège. Société Royale des Sciences de Liège. Mémoirs. Brussels.
Mém. Soc. Russe Min. Mémoires de la Société Russe de Minéralogie. Moscow.
Mém. Soc. Sci. Liège. Mémoires de la Société des Sciences de Liège. Liège.
Mém. Soc. Sci. Phys. Nat. Bordeaux. Mémoires de la Société des Sciences Physiques et Naturelles de Bordeaux. Bordeaux.
Mem. Soc. Spettroscop. Memorie della Società degli Spettroscopisti Italiana. Catania.
Mém. Soc. Vaud. Mémoires de la Société Vaudoise des Sciences Naturelles. Lausanne.
Messenger of Math. Messenger of Mathematics. Cambridge.
Met. Abstr. Metallurgical Abstracts. London.
Met. Chem. Eng. Metallurgical and Chemical Engineering. New York.
Met. Ital. Metallurgia Italiana. Milan.
Met. Periodic Rev. Metallgesellschaft. Periodic Review.
Metal Abs. Metallurgical Abstracts. London.
Metal Finishing. Westwood. N. Jersey.
Metal Ind. The Metal Industry. London.
Metal. Ind. Co. Chem. Abs. The Metal Industry Co. Chemical Abstracts.
Metal Ind. (*London*). The Metal Industry and the Iron Foundry. London.
Metal Ind. (*New York*). The Metal Industry. New York.
Metal Progr. Metal Progress. Novelty, Ohio.
Metal Trans. Metal Transactions. London.
Metal Treatment. London.
Metalen. Technisch-Wetenschappelijk en Industreël Tijdschrift. The Hague.
Metall. Grünewald.
Metall u. Erz. Metall und Erz. Halle.
Metallbörse. Berlin.
Metallforsch. Metallforschung. Stuttgart.
Metalloberfläche. Munich.
Metallographist. Boston.
Metals and Alloys. Easton, Pa.
Metals Tech. Metals Technology. American Institute of Mining and Metallurgical Engineers. Technical Publication. New York.
Metallurgia. Manchester.
Metallurgia Italiana. Milan.
Metallurgie. Halle.
Metallurgie u. Giessereitech. Metallurgie und Giessereitechnik.
Metallurgist. London.
Metallwirtsch. Metall-Wirtschaft, Wissenschaft, Technik. Berlin.
Métaux. (*Corrosion-Inds.*). Combination of Métaux & Corrosion and Métaux & Industries. St. Germain.
Meteorol. Rundschau. Meteorologische Rundschau. Berlin.
Meteorol. Z. Meteorologische Zeitschrift. Brunswick.
Metody i Protsessy Khim. Tekhnol. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk Sbornik. Metody i Protsessy Khimicheskoi Tekhnologii, Akademiya Nauk S.S.S.R., Otdelenie Khimicheskikh Nauk, Sbornik. Moscow.
Metody Issl. Keram. Mat.
Metropol. Mus. (*New York*) *Report.* Metropolitan Museum Report. New York.

Mezögazdasági Kutatások. Budapest.

Mfg. Chem. Manufacturing Chemist, and Pharmaceutical, Cosmetic and Photographic Trade Journal. London.

Microbiol. Españ. Microbiologia Española. Madrid.

Mikrobiol. Zhur., Akad. Nauk Ukr. R.S.R. Microbiologichnii Zhurnal, Akademiya Nauk Ukrains'koi R.S.R.

Mikrobiologiya. Moscow.

Mikrochem. Mikrochemie. Vienna.

Mikrochem. Emich Festschr. Mikrochemie Emich Festschrift.

Mikrochemie ver. Mikrochem. Acta. Mikrochemie vereinigt mit Mikrochimica Acta. Vienna.

Mikrochim. Acta. Mikrochimica Acta. Vienna.

Mikrokosmos. Stuttgart.

Milchw. Forsch. Milchwirtschaftliche Forschungen.

Milchwissenschaft. Nuremburg.

Min. Agr. Dept. N.P. Min. Ministério da Agricultura, Departmento Nacional da Produção Mineral. Rio de Janeiro.

Min. and Met. Invest. U.S. Bur. Mines Carnegie Inst. Boards. Mining and Metallurgical Investigations under the Auspices of the U.S. Bureau of Mines. Carnegie Institute of Technology and Mining and Metallurgical Advisory Boards. Pittsburg, Pa.

Min. Mag. Mining Magazine. Denver, Colo.

Min. Petr. Mitt. Mineralogische und Petrographische Mitteilungen. Leipzig, Vienna.

Mine and Quarry Eng. Mine and Quarry Engineering. London.

Miner. Ind. Mineral Industry. New York.

Mineração e Mat. (Rio de J.). Mineração e Metalurgia (Rio de Janeiro).

Mineral. Mag. The Mineralogical Magazine and Journal of the Mineralogical Society. London.

Mineral. Syr'. Mineral'noe Syr'e. Moscow.

Minéraln. Oudobr. Minéral' nye Udobrenija i Insektofungisidy.

Mineralog. Abstr. Mineralogical Abstracts. London.

Minerva Med. Minerva Medica. Turin.

Minerva Pediat. Minerva Pediatrica. Turin, Italy.

Mining and Met. Mining and Metallurgy. New York.

Mining Congress J. Mining Congress Journal. Washington.

Mining Eng. Mining Engineering. New York.

Mining J. (London). Mining Journal. London.

Mining J. (Moscow). Mining Journal. Moscow.

Mining Mag. Mining Magazine. London.

Misc. Phys. and Chem. Techniques. Miscellaneous Physical and Chemical Techniques. London.

Misc. Publ. Miscellaneous Publications (of the International Tin Research and Development Council). Middlesex, England or Columbus, Ohio.

Mises au point chim. anal. pure et appl. et anal. bromatol. Mises au point de chimie analytique pure et appliquée et d'analyse bromatologique. Paris.

Missouri Agr. Exptl. Sta. Ann. Rep. Missouri Agricultural Experimental Station. Annual Report. Columbia, Mo.

Missouri Univ. School Mines and Met. Bull. Tech. Ser. University of Missouri, School of Mines and Metallurgy Bulletin, Technical Series. Rolla.

Mitt. Chem. Forsch. Inst. Ind. Österr. Mitteilungen des Chemischen Forschungs-Institutes der Industrie Österreichs. Vienna.

Mitt. deut. Landw. Ges. Mitteilungen der deutschen Landwirtschafts-Gesellshaft. Frankfurt a.M.

Mitt. deut. Materialprufungsanstalt. Mitteilungen der deutschen Materialprufungsanstalten. Frankfurt a.M.

Mitt. K. Wilh. Inst. Eisenforsch. Mitteilungen aus dem Kaiser Wilhelm-Institut für Eisenforschung Düsseldorf. Düsseldorf.

Mitt. Kali-Forsch. Anst. Mitteilungen der Kali-Forschungs-Anstalt.

Mitt. Kältetechn. Inst. Karlsruhe. Mitteilungen des Kältetechnischen Instituts. Karlsruhe.

Mitt. Kgl. Materialsprüfungsamt. Mitteilungen aus dem Königlichen Materialsprüfungsamt zu Gross-Lichtenfelde. Berlin-Dahlem.

Mitt. Lab. Preuss. Land. Mitteilungen aus den Laboratorien der preussischen geologischen Landesanstalt.

Mitt. Lebesm. Hyg. Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene. Bern.

Mitt. Materialsprüfungsamt K. Wilh. Inst. Metallforsch. Mitteilungen aus dem Materialsprüfungsamt und dem Kaiser Wilhelm-Institut für Metallforschung zu Berlin-Dahlem. Berlin.

Mitt. Med. Akad. Kioto. Mitteilungen aus der Medizinischen Akademie zu Kioto. Kyoto, Japan.

Mitt. Reichsinst. Forst. u. Holz. Mitteilungen des Reichsinstituts für Forst- und Holzwirtschaft.

Mitt. Ver. Grosskesselbesitzer. Mitteilungen der Vereinigung der Grosskesselbesitzer. Düsseldorf, Germany.

Mitt. Versuchssta. Gaerungsgewerbe Inst. Angew. Mikrobiol. Mitteilungen der Versuchsstation für das Gaerungsgewerbe sowie des Instituts für Angewandte Mikrobiologie und der Dozentur für Lagertechnik und Vorratsschutz der Hochschule für Bodenkultur in Wien. Vienna.

Mod. Metals. Modern Metals. Chicago.

Modern Brewer. Chicago.

Modern Plastics. New York.

Modern Refrig. Modern Refrigeration. London.

Modern Trends in Physiol. and Biochem. Modern Trends in Physiology and Biochemistry. New York.

Mokuzai Kenkyu. (Wood Research) Kyoto.

Molochnaya Prom. Molochnaya Promyshlennost. (Dairy Industry). Moscow.

Mon. Pétrole Roumain. Moniteur du Pétrole Roumain. Bucharest.

Mon. Sci. Moniteur Scientifique du Docteur Quesneville. Paris.

Monatsh. Monatshefte für Chemie und verwandte Teile anderer Wissenschaften. Vienna.

Monatsh. Math. Phys. Monatshefte für Mathematik und Physik. Vienna.

Monde Ind. Monde Industriel. Ghent.

Monit. Ostet.-Ginecol. Monitore Ostetrico-Ginecologico. Modena.

Montan. Rundschau. Montanistische Rundschau.

Month. Not. Astron. Soc. S. Africa. Monthly Notices of the Astronomical Society of South Africa.

Month. Not. Roy. Astron. Soc. Monthly Notices of the Royal Astronomical Society. London.

Mosskulturforenhingens Svenska Tids. Mosskulturforenhingens Svenska Tijdschrift och Mosskveturföreningens Meddelanden.

Münch. Med. Woch. Münchener Medizinische Wochenschrift. Munich.

Munic. Eng. Municipal Engineering. Chicago.

Munic. Eng. Sanit. Record. Municipal Engineering, Sanitary Record and Municipal Motor. London.

Munich. Ber. Sitzungsberichte der Königlichen Bayerischen Akademie der Wissenschaften zu München. Mathematisch-Physikalische Klasse. Munich.

Myasnaya Ind. S.S.S.R. Myasnaya Industriya S.S.S.R. (Meat Industry). Moscow.

Mysore Agr. J. Mysore Agricultural Journal. Bangalore.

N. Engl. J. Med. New England Journal of Medicine. Boston, Mass.

N.J. der Phys. Neues Journal der Physik. Leipzig.

N. Jahrb. Min. Neues Jahrbuch für Mineralogie, Geologie und Paläontologie. Stuttgart.

N. Jahrb. Min. Abhl. Neues Jahrbuch für Mineralogie. Abhandlungen. Section A. Stuttgart.

N. Jahrb. Min. B. Bd. Neues Jahrbuch für Mineralogie etc. Beilage Band. Stuttgart.

N. Jahrb. Min. Monatsh. Neues Jahrbuch für Mineralogie. Monatsheft. Stuttgart.

N. Mém. Acad. Berlin. Nouveaux Mémoires de l'Académie Royale des Sciences et des Belles-Lettres de Berlin. Berlin (1770-86).

N.N.E. National Nuclear Energy Series, Manhatten Project Technical Station. New York.

N.S.A. Nuclear Science Abstracts. New York.

N.Y. State Med. J. New York State Journal of Medicine. Easton, Pa.

N. Zeal. J. Sci. Tech. New Zealand Journal of Science and Technology. Wellington.

Nachr. Akad. Wiss. Göttingen, Math.-Phys. Klasse IIa. Math.-Phys.-Chem. Abt. Nachrichten der Akademie der Wissenschaften in Göttingen, Mathematisch-Physikalische Klasse IIa. Mathematisch-Physikalisch-Chemische Abteilung. Göttingen.

Nachr. Ges. Wiss. Göttingen. Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen. Göttingen.

Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse, Fachgruppe II. Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse, Fachgruppe II. Göttingen.

Nachr. Phys. Chem. Lab. Semsoinsés. Nachrichten von der Physikalische-Chemische Laboratory. Semsoinsés.

Nafta. (Petroleum). Zagreb.

Nanking J. Nanking Journal. Nanking.

Nat. Advisory Comm. Aeronaut. National Advisory Committee for Aeronautics. Washington.

Nat. Eng. National Engineer. Chicago.

Nat. Nuclear Energy Ser. National Nuclear Energy Series. Manhatten Project Technical Section. New York.
Nat. Petrol. News. National Petroleum News. New York.
Nat. Sci. Rep. Ochanomizu Univ.
Natl. Res. Council Can. National Research Council of Canada. Ottawa.
Natur u. Volk. Natur und Volk. Frankfurt a.M.
Natural Gas and Gasoline J. Natural Gas and Gasoline Journal. Buffalo.
Natural Gases U.S.S.R. Moscow.
Nature. London.
Naturw. Sammlung. Naturwissenschaftliche Sammlung. Stuttgart.
Naturwiss. Die Naturwissenschaften. Berlin.
Naturwiss. Rundsch. Naturwissenschaftliche Rundschau. Stuttgart.
Natuurw. Tijdschr. Natuurwetenschappelijk Tijdschrift. Ghent.
Natuurw. Tijdschr. Nederland-Indië. (later Chronica Naturæ.)
Nauch. Agron. Zhur. Nauchno Agronomicheskiĭ Zhurnal. Moscow.
Nauk. Zapiski Tzukrovoï Prom. Naukovi Zapiski s Tzukrovoï Promislovosti.
Nauk. Zapysky L'vov. Derzhavnogo Univ. im. Ivana Franka. Naukovi Zapiski, L'vovs'kiĭ Derzhavniĭ Universitet imeni Ivana Franka. Lvov, Ukr. S.S.R.
Naunyn-Schmiedeberg's Arch. exptl. Path. Pharmakol. Naunyn-Schmiedeberg's Archiv für Experimentelle Pathologie und Pharmakologie. Berlin.
Nederl. Tijdschr. Geneeskunde. Nederlandsch Tijdschrift voor Geneeskunde. Haarlem.
Nederl. Tijdschr. Natuurkde. Nederlandsch Tijdschrift voor Natuurkunde. The Hague.
Neft. (Petroleum). Moscow.
Néoplasmes (*Paris*). Paris.
Nernst Festschr. Nernst Festschrift.
Nervenarzt. Berlin.
Neues Jahrb. Mineral. Geol. Neues Jahrbuch für Mineralogie, Geologie und Paläontologie. Stuttgart.
Neues Jahrb. Mineral. Geol. Beil. Bd. Neues Jahrbuch für Mineralogie, Geologie und Paläontologie. Beilage Band. Stuttgart.
Neurology. Minneapolis, Minn.
New England J. Med. New England Journal of Medicine. Boston, Mass.
New Jersey Agr. Expt. Sta. Bull. New Jersey Agricultural Experiment Station Bulletin. New Brunswick, N.J.
New Mex. Mines Min. Res. New Mexico, Bureau of Mines and Mineral Resources, Bulletin. Sorocco, N.M.
New Phytol. New Phytologist. Cambridge.
New Zealand J. Agr. New Zealand Journal of Agriculture. Wellington.
New Zealand J. Sci. Tech. New Zealand Journal of Science and Technology. Wellington.
Nicholson's J. Nicholson's Journal. London.
Nickel Bull. Nickel Bulletin. London.
Nippon Kin. Gakkai-Shi. Nippon Kinzoku Gakkai-Shi. Sendai City, Japan.
Nisshin Igaku. Tokyo.
Nitrocellulose. Berlin.
Nord. Kemikermøde, Förh. Nordiske Kemikermøde, Förhandlingar. Oslo.
Nord. Kjemi. Nordiske Kjemikermøte. 4th Meeting, Oslo, 1932.
Nord. Med. Nordisk Medicin. Stockholm.
Norg. Geol. Undersökels. Norges Geologiske Undersökelse. Oslo.
Norsk Geol. Tijdsskr. Norsk Geologisk Tidsskrift. Oslo.
Norsk Mag. Laegev. Norsk Magasin for Laegevidenskapen.
Norsk Skogind. Norsk Skogindustri. Oslo.
Northwest Sci. Northwest Science. Moscow, Idaho.
Noticias Farm. Noticias Farmacêuticas. Coimbra.
Notiz. chim.-ind. Notiziario Chimico-industriale. Milan.
Nouv. Mém. Acad. Berlin. (See *N. Mem. Acad. Berlin*).
Nouv. Mém. Soc. Imp. Nat. Moscou. Société Impériale des Naturalistes de Moscou. Nouveaux Mémoires. Moscow.
Nova Acta Leopold. Nova Acta Academiae Caesareae Leopoldina-Carolinae Germanicae Naturae Curiosorum. Halle.
Nova Acta Soc. Reg. Uppsal. Nova Acta Regiae Societatis Scientiarum Upsaliensis. Uppsala.
Nova Proizvodnja. (New Production). Ljubljana.
Novi Comment. Acad. Petropol. Novi Commentarii. Académie Impériale des Sciences de St. Petersbourg. St. Petersburg (1747-75).

Novosti Neftyanoĭ Tekh. Neftepromyslovoe Delo. Novosti Neftyanoĭ Tekhniki. Neftepromyslovoe Delo. Moscow.
Novosti Tekh., Ser. Gornorudnaya Prom. Novosti Tekhniki, Series, Gornorudnaya Promyshlennost. Moscow.
Nuclear Eng. Nuclear Engineering. London.
Nuclear Phys. Nuclear Physics. New York.
Nuclear Sci. Abstr. Nuclear Science Abstracts. New York.
Nuclear Sci. and Eng. Nuclear Science and Engineering. New York, London.
Nucleonics. New York.
Nuov. Cim. Il Nuovo Cimento. Bologna.
Nuova Giorn. Botan. Ital. Nuova Giornale Botanico Italiano. Florence.
O.R.N.L. Oak Ridge National Laboratory. Reports.
Obs. sur la Phys. Observations sur la Physique, sur l'Histoire Naturelle et sur les Arts. Paris.
Observatory. Herstmonceux, Sussex.
Obstet. Gynecol. Survey. Obstetrical and Gynecological Survey. Baltimore, Md.
Occupational Hazards. Cleveland, Ohio.
Oefversigt af K. Vetensk. Akad. Förhandl. Oefversigt af K. Vetenskaps Akademiens Förhandlingar. Stockholm.
Official Gaz. Official Gazette. Washington, D.C.
Official Proc. Master Boilermakers' Assoc. Official Proceedings of the Master Boilermakers' Association. New York.
Ofv. Finska Vet. Soc. Förhl. Ofversigt af Finska Vetenskaps-Societetens Förhandlingar. Helsinki.
Ogneupory. (Refractories). Moscow.
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Ohio Eng. Expt. Stat. Bull. Ohio State University. Engineering Experiment Station Bulletin. Columbus, Ohio.
Ohio J. Sci. Ohio Journal of Science. Columbus, Ohio.
Ohio State Univ. Eng. Expt. Stat. News. Ohio State University. Engineering Experiment Station News. Columbus, Ohio.
Ohio State Univ. Stud. Ohio State University Studies. Columbus, Ohio.
Oil and Soap. Chicago.
Oil Eng. Finance. Oil Engineering and Finance.
Oil Gas J. Oil and Gas Journal. Tulsa, Okla.
Oil Ind. U.S.S.R. Oil and Fat Industry. Moscow.
Oil Weekly. (See *World Oil*). Houston, Texas.
Oklahoma Agr. Expt. Sta. Bull. Oklahoma Agricultural Experiment Station, Bull. Stillwater, Okla.
Öl u. Kohle. Öl und Kohle. Berlin.
Oléagineux. Paris.
Onderz. Physiol. Scheikunde. Onderzoekingen van Physiologische Scheikunde.
Onderzoekingen Physiol. Lab., Utrecht. Onderzoekingen van den Physiologische Laboratorium. Utrecht.
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Optika i Spectroskopiya. Moscow.
Optiko-Mekhan. Prom. Optiko-Mekhanicheskaya Promyshlennost. Moscow.
Ordnance. Washington.
Org. Chem. Ind. U.S.S.R. Organic Chemical Industry. Moscow, U.S.S.R.
Organic Reactions. New York.
Orv. Lap Nép. Orvosok Lapja Népegésgségugy. Budapest.
Orvosi Hetilap. (Medical Weekly) Budapest.
Osiris. Bruges.
Österr. Akad. Wiss. Österreichische Akademie der Wissenschaften. Vienna.
Österr. Akad. Wiss., Math.-Naturw. Klasse, Anz. Österreichische Akademie der Wissenschaften, Mathematisch-Naturwissenschaftliche Klasse, Anzeiger. Vienna.
Österr. Chem. Ztg. Österreichische Chemiker-Zeitung. Vienna.
Österr. Leder-Ztg. Österreichische Leder-Zeitung. Vienna.
Ostwald's Klassiker. Ostwald's Klassiker der Exakten Wissenschaften. Leipzig.
Ov. K. Dansk. Videns. Selsk. Forhl. Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger. Copenhagen.
Oxford Sci. Oxford Science. Oxford.
Ôyô Butsuri (*Journal of Applied Physics.*). Tokyo.

Pacific Chem. Met. Ind. Pacific Chemical and Metallurgical Industries. San Francisco.
Pacific Fisherman Year Book. Washington.
Pacific Pulp Paper Ind. Pacific Pulp and Paper Industry. San Francisco.
Paint, Oil Chem. Rev. Paint, Oil, & Chemical Review. Chicago.
Pakistan J. Sci. Res. Pakistan Journal of Scientific Research. Lahore, Pakistan.
Palestine J. Botany. Rehovot, Israel.
Paliva a Voda. (Fuel & Water). Prague.
Paper. New York.
Paper Ind. Paper Industry. Chicago, Illinois.
Paper Ind. and Paper World. Paper Industry and Paper World. Chicago, Illinois. (See *Paper Ind.*).
Paper Makers' Monthly J. Paper Makers' Monthly Journal.
Paper Mill. Paper Mill and Wood Pulp News. New York.
Paper Mill News. New York.
Paper Trade J. Paper Trade Journal. New York.
Paperi ja puu. Helsinki.
Papeterie. Paris.
Papier-Fabr. Der Papier-Fabrikant. Württemberg.
Papir-J. Papir-Journalen. Oslo.
Pediat. Intern. Pediatria Internazionale. Rome.
Pediatria (Naples). Naples.
Pediatrics. Springfield, Ill.
Pedology U.S.S.R. Moscow.
Pennsylvania Expt. Sta., Bull. Pennsylvania Experiment Station, Bulletin. Univ. Park.
Perfumery Essent. Oil Record. Perfumery and Essential Oil Record. London.
Periodico Minerale. Periodico di Mineralogia. Rome.
Pests. Pests and their Control. Cleveland, Ohio.
Petrol. Refiner. Petroleum Refiner. Houston, Tex.
Petrol. Times. Petroleum Times. London.
Petroleum. London.
Petroleum Engr. The Petroleum Engineer. Dallas, Tex.
Petroleum (German), Petrol. Z. Petroleum Zeitschrift für die gesamte Interesse der Mineralöl-Industrie. Berlin.
Petroleum Processing. New York.
Pflanzenbau. Vienna.
Pharm. Acta Helv. Pharmaceutica Acta Helvetiae. Zürich.
Pharm. Bull. (Japan). Pharmaceutical Bulletin. Tokyo.
Pharm. J. Pharmaceutical Journal. London.
Pharm. Presse. Pharmazeutische Presse.
Pharm. Tijd. Neder. Ind. Pharmaceutisch Tijdschrift voor Nederlandsch-Indië. Antwerp.
Pharm. Weekbl. Pharmaceutisch Weekblad voor Nederland. Amsterdam.
Pharm. Zentralhalle. Pharmazeutische Zentralhalle für Deutschland. Dresden.
Pharm. Ztg. Pharmazeutische Zeitung. Frankfurt a.M.
Pharmacia. Estonia.
Pharmacol. Revs. Pharmacological Reviews. Baltimore.
Pharmazie. Berlin.
Phil. Mag. Philosophical Magazine. London.
Phil. Trans. Philosophical Transactions of the Royal Society. London. Section A unless B stated.
Phil. Trans. Abdgd. Philosophical Transactions. 18 vols., London, 1809.
Philipp. J. Sci. Philippine Journal of Science. Manila.
Philippine Agriculturist. Laguna, Philippine Islands.
Philips Research Rep. Philips Research Reports. Eindhoven.
Philips Tech. Rundschau. Philips Technische Rundschau. Eindhoven.
Philips Technical Review. Eindhoven.
Phosphorsäure. Essen.
Phot. Chronik. Photographische Chronik. Halle.
Phot. Ind. Photographische Industrie. Berlin.
Phot. Ind. (Japan). Photographic Industries. Tokyo.
Photo Rev. Photo Revue. Paris.
Photogr. J. Photographic Journal. London.
Photographe. Paris.
Phys. Ber. Physikalische Berichte. Berlin.

Phys. Regel. Ber. Die Physik in regelmässigen Berichten. Leipzig.
Phys. Rev. Physical Review. New York.
Phys. Rev. Suppl. Physical Review Supplement. New York.
Phys. Z. Physikalische Zeitschrift. Leipzig.
Phys. Z. Sowjet. Physikalische Zeitschrift der Sowjetunion.
Physica. Utrecht.
Physical Memoirs (*Phys. Soc.*). Physical Memoirs. Physical Society. London.
Physics. New York.
Physiol. Abstr. Physiological Abstracts. London.
Physiol. Rev. Physiological Reviews. Washington, D.C.
Physiol. Plantarum. Physiologia Plantarum. Copenhagen.
Phytiat.-Phytopharm. Phytiatrie-Phytopharmacie. Paris.
Phytomorphology. Delhi.
Phytopath. Z. Phytopathologische Zeitschrift. Hamburg.
Phytopathology. Baltimore, Mo.
Pishchevaya Prom. Pishchevaya Promyshlennost. Moscow.
Pitture e Vernici. Milan.
Plansee Proc. Plansee Proceedings. London.
Plant and Soil. The Hague.
Plant Physiol. Plant Physiology. Kutztown, Pa.
Planta. Berlin.
Planter Sugar Mfr. Planter and Sugar Manufacturer. London.
Plastica. Schiedam, Holland.
Plating. Newark, N.J.
Pochvovednie. (Soil Science). Moscow.
Pogg. Ann. (See Ann. Phys).
Policlinico, Sez. Med. La Policlinico (Rome), Sezione Medica. Rome.
Policlinico, Sez. Prat. La Policlinico, Sezione Pratica. Rome.
Poligraf. Proizvodstvo. Poligraficheskoe Proizvodstvo. (Printing Trade). Moscow.
Polish Agr. Forest Ann. Polish Agricultural and Forest Annual. Poznan.
Polska Akad. Umiejetności. Polska Akademia Umiejetności. Cracow.
Polytech. Tijdschr. Polytechnisch Tijdschrift. Heemstede, Holland.
Polytechn. Weekbl. Polytechnisch Weekblad. Amsterdam.
Poona Agr. Coll. Mag. Poona Agricultural College Magazine. Poona, India.
Poultry Sci. Poultry Science. College Station, Tex.
Powder Met. Bull. Powder Metallurgy Bulletin. Yonkers, N.Y.
Power. New York.
Power Generation. New York.
Power Plant Eng. Power Plant Engineering. Chicago.
Power Works Engr. Power and Works Engineer. London.
Poznañaya Tekh. Poznañaya Tekhnika.
Poznań. Towarz. Przyjaciół Nauk, Prace Komisji Med. Doświadczalnej. Poznańskie Towarzystwo Przyjaciół Nauk, Prace Komisji Medycyny Dóswiadczalnej. Poznań, Poland.
Prace Głównego Inst. Chem. Przemysl. Prace Głównego Instytutu Chemii Przemyslowej. Stalinogród, Poland.
Prace Głównego Inst. Gornictwa, Komun. Prace Głównego Instytutu Gornictwa, Komunikat. Katowice, Poland.
Prace Inst. Mech. Met. (Nowe Prace Instytute Mechaniki Precyzyjne.) Warsaw.
Prace Inst. Ministerstwa Hutnictwa. Prace Instytutow Ministerstwa Hutnictwa. Stalinogród, Poland.
Prace Placówek Nauk-Badawcz. Ministerstwa Przemystu Chem. Prace Placówek Naukowo-Badawczych Ministerstwa Przemystu Chemicznego. Warsaw.
Prakt. Chem. Praktische Chemie. Vienna.
Praktika Akad. Athenon. Praktika tes Akademias Athenon. Athens.
Praktiký Lékař. Prague.
Presse Méd. Presse Médicale. Paris.
Priroda. (Nature). Leningrad.
Problems Sov. Geol. Problems of Soviet Geology. Leningrad, Moscow.
Problemy Endokrinol. Problemy Endokrinologii. Moscow.
Problemy Kinetiki i Kataliza, Sbornik Trudov Konferentsii Posvyashchennă Sorokaletiyu. Perekisnoĭ Teorii Bakhol-Engles. Moscow.
Proc. Acad. Sci. Amst. Proceedings of the Royal Academy of Sciences of Amsterdam. Amsterdam.

Proc. Amer. Acad. Proceedings of the American Academy of Arts and Sciences. Boston.

Proc. Amer. Assoc. Textile Chem. Colorists. Proceedings of the American Association of Textile Chemists and Colorists. New York.

Proc. Amer. Electroplaters' Soc. Proceedings of the Technical Sessions of the Annual Convention of the American Electroplaters' Society. Jenkintown, Pa.

Proc. Amer. Gas Assoc. Proceedings of the American Gas Association. New York.

Proc. Amer. Petrol. Inst. Proceedings of the American Petroleum Institute. New York.

Proc. Amer. Petrol. Inst., 17th Mid-Year Meeting. New York. Proceedings of the American Petroleum Institute. New York.

Proc. Amer. Phil. Soc. Proceedings of the American Philosophical Society. Philadelphia.

Proc. 8th. Amer. Sci. Congr. Geol. Sci. Proceedings of the 8th. American Scientific Congress. Geological Sciences. Washington.

Proc. Amer. Soc. Animal Production. Proceedings of the Annual Meeting of the American Society of Animal Production. Illinois.

Proc. Amer. Soc. Brewing Chemists. Proceedings of the American Society of Brewing Chemists. Madison, Wis.

Proc. Amer. Soc. Hort. Sci. Proceedings of the American Society for Horticultural Science. Ithaca, N.Y.

Proc. Amer. Soc. Sugar Beet Technol. Proceedings of the American Society of Sugar Beet Technologists. New York.

Proc. Amer. Soc. Testing Mat. Proceedings of the American Society for Testing Materials. Easton, Pa.

Proc. Amer. Wood-Pres. Assoc. Proceedings of the American Wood-Preservers' Association. Washington.

Proc. and Trans. Rhodesia Sci. Assoc. Rhodesia Scientific Association. Proceedings and Transactions. Salisbury, S. Rhodesia.

Proc. 21st. Ann. Conv. Sugar Technol. Assoc. India. Proceedings of the 21st. Annual Convention of the Sugar Technologists' Association. India.

Proc. Brit. Assoc. Refrig. Proceedings of the British Association of Refrigeration. London.

Proc. Brit. Inst. Refrig. Proceedings of the British Institute of Refrigeration. London.

Proc. Brit. West Indies Sugar Technol. Kingston.

Proc. Cambr. Phil. Soc. Proceedings of the Cambridge Philosophical Society. Cambridge.

Proc. Chem. Soc. Proceedings of the Chemical Society. London.

Proc. Chem. Specialties Mfrs. Assoc. Proceedings of the Chemical Specialties Manufacturers' Association. Canton.

Proc. Conf. Nuclear Meson Phys. Proceedings of the Conference on Nuclear and Meson Physics, Glasgow, London and New York.

Proc. Congr. Pure and Appl. Chem., London. Proceedings of the Congress on Pure and Applied Chemistry. London.

Proc. Durham Phil. Soc. Proceedings of the Durham Philosophical Society. Durham.

Proc. Edin. Math. Soc. Proceedings of the Edinburgh Mathematical Society. Edinburgh.

Proc. Imp. Acad. Japan. Proceedings of the Imperial Academy of Japan. Tokyo.

Proc. Indian Acad. Proceedings of the Indian Academy of Sciences. Bangalore.

Proc. Indian Assoc. for Cultivation of Science. Proceedings of the Indian Association for the Cultivation of Science. Calcutta.

Proc. XV Indian Sci. Congr. Proceedings of the XV Indian Science Congress. Calcutta.

Proc. Indiana Acad. Sci. Proceedings of the Indiana Academy of Science. Indianapolis, Indiana.

Proc. Inst. Brit. Foundrymen. Proceedings of the Institute of British Foundrymen. Manchester.

Proc. Inst. Chem. India. Proceedings of the Institution of Chemists. India.

Proc. Inst. Civ. Eng. Proceedings of the Institution of Civil Engineers. London.

Proc. Inst. Mech. Eng. Proceedings of the Institution of Mechanical Engineers. London.

Proc. Inst. Met. Div. Amer. Inst. Met. Eng. Proceedings of the Institute of Metals Division. American Institute of Mining and Metallurgical Engineers. New York.

Proc. XI Int. Congr. Pure and Appl. Chem. Proceedings of the Eleventh International Congress of Pure and Applied Chemistry. London, 1947.

Proc. Intern. Assoc. Testing Mat. Proceedings of the International Association for Testing Materials. London.

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Proc. 13th. Intern. Dairy Congr. (Hague). Proceedings of the 13th. International Dairy Congress. The Hague.

Proc. Intern. Seed Testing Assoc. Proceedings of the International Seed Testing Association. Copenhagen.

Proc. Internat. Congr. Refrig. (See *Internat. Congr. Refrig.*).
Proc. Internat. Soc. Soil Sci. Proceedings of the International Society of Soil Science.
Proc. Internat. Symposium Reactivity of Solids, Gothenburg. Proceedings of the Internationa Symposium on the Reactivity of Solids. Gothenburg.
Proc. Iowa Acad. Proceedings of the Iowa Academy of Science. Des Moines.
Proc. Japan Acad. Soc. Proceedings of the Japan Academy of Science. Tokyo.
Proc. K. Akad. Wetens. Amsterdam. Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings of the Section of Sciences. Amsterdam.
Proc. Leeds Phil. Soc. Proceedings of the Leeds Philosophical and Literary Society. Leeds.
Proc. Lenin Acad. Agr. Sci. (*U.S.S.R.*). Proceedings of the Lenin Academy of Agricultural Sciences, U.S.S.R. Moscow.
Proc. Leningrad Inst. Dept. Fert. Proceedings of the Leningrad Institution. Department for Fertilisers.
Proc. Linnean Soc. N.S. Wales. Proceedings of the Linnean Society of New South Wales, Sydney.
Proc. London Math. Soc. Proceedings of the London Mathematical Society. London.
Proc. 6th. Meeting Intern. Comm. Electrochem. Thermodynam. and Kinet. Proceedings of the 6th Meeting of the International Committee of Electrochemical Thermodynamics and Kinetics. London.
Proc. N.B.S. Semicentennial Symposium Low-Temp. Phys. Nat. Bur. Stand. Proceedings of the National Bureau of Standards. Semicentennial Symposium Low-Temperature. Physics.
Proc. Nat. Acad. Proceedings of the National Academy of Sciences of the United States of America. Washington.
Proc. Nat. Acad. Sci. India. Proceedings of the National Academy of Science, India. Allahabad.
Proc. Nat. Electron. Conf. Proceedings of the National Electronics Conference. Chicago.
Proc. Nat. Inst. Sci. India. Proceedings of the National Institute of Sciences of India. New Delhi.
Proc. Nutr. Soc. Proceedings of the Nutrition Society. Cambridge.
Proc. Oklahoma Acad. Sci. Proceedings of the Oklahoma Academy of Science. Norman, Oklahoma.
Proc. 7th. Pacific Sci. Congr., New Zealand. Proceedings of the 7th. Pacific Science Congress, New Zealand.
Proc. Pacific Sci. Congr. Pacific Sci. Assoc. Proceedings of the Pacific Science Congress of the Pacific Science Association. Berkeley, Calif.
Proc. Penna. Acad. Proceedings of the Pennsylvania Academy of Sciences. Harrisburg, Pennsylvania.
Proc. Phil. Soc. Glasgow. Proceedings of the Philosophical Society of Glasgow. Glasgow.
Proc. Phys. Math. Soc. Japan. Proceedings of the Physico-Mathematical Society of Japan. Tokyo.
Proc. Phys. Soc. Proceedings of the Physical Society. London.
Proc. Phys. Soc. Japan. Proceedings of the Physical Society of Japan. Tokyo.
Proc. Roy. Acad. Amsterdam. Proceedings of the Royal Academy of Amsterdam.
Proc. Roy. Dublin Soc. The Scientific Proceedings of the Royal Dublin Society. Dublin.
Proc. Roy. Inst. Proceedings of the Royal Institution of Great Britain. London.
Proc. Roy. Irish Acad. Proceedings of the Royal Irish Academy. Dublin.
Proc. Roy. Soc. Proceedings of the Royal Society. London.
Proc. Roy. Soc. Edin. Proceedings of the Royal Society of Edinburgh. Edinburgh.
Proc. Roy. Soc. Med. Proceedings of the Royal Society of Medicine. London, New York.
Proc. Roy. Soc. N.S. Wales. (See *J. Proc. Roy. Soc. N.S. Wales*).
Proc. S. African Sugar Technol. Assoc. Proceedings of the South African Sugar Technologists' Association. Johannesburg.
Proc. S. Dakota Acad. Sci. Proceedings of the South Dakota Academy of Science. Vermillion, South Dakota.
Proc. Sci. Assoc., Maharajah's College Vizianagram. Proceedings of the Scientific Association, Maharajah's College, Vizianagram.
Proc. Soc. Appl. Bact. Proceedings of the Society for Applied Bacteriology. London.
Proc. Soc. Chem. Ind. Victoria. Proceedings of the Society of Chemical Industry. Victoria.
Proc. Soc. Exp. Biol. Med. Proceedings of the Society for Experimental Biology and Medicine. New York.
Proc. Soc. Promotion Agr. Sci. Proceedings of the Annual Meeting of the Society for the Promotion of Agricultural Science.
Proc. Soil Sci. Amer. Soil Science Society of America. Proceedings. Ann Arbor.

Proc. Staff Meetings Mayo Clinic. Rochester, Minn., U.S.

Proc. State Coll. Wash. Inst. Dairyg. Proceedings of the State College of Washington. Institute of Dairying. Pullman, Wash.

Proc. Sugar Technol. Assoc., India. Proceedings of the Sugar Technologists' Association. Kanpur, India.

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Proc. Trans. Nova Scot. Inst. Sci. Proceedings and Transactions of the Nova Scotian Institute of Science. Halifax, N.S.

Proc. Utah Acad. Sci. Proceedings of the Utah Academy of Sciences, Arts, and Letters. Logan, Utah.

Proc. Wash. Acad. Proceedings of the Washington Academy of Science. Washington.

Proc. World Eng. Cong. Tokyo 1929. Proceedings of the World Engineering Congress. Tokyo, 1929.

Proc. Yale Mineralog. Soc. Proceedings of the Yale Mineralogical Society.

Proc. Yorkshire Geol. Soc. Proceedings of the Yorkshire Geological Society. Leeds.

Proc. Zeeman Congr. Amsterdam. Proceedings of the Zeeman Congress, Amsterdam.

Producers' Monthly. Bradford, Pa.

Product. Eng. Product Engineering. New York.

Progr. Agr. Vit. Progrès Agricole et Viticole. Montpellier.

Progr. Med. Progresso Medico. Naples.

Progr. Nuclear Phys. Progress in Nuclear Physics. London.

Progr. Theor. Phys. Progress of Theoretical Physics. Kyoto.

Prometheus. Leipzig.

Protar. Solothurn, Switz.

Protoplasma. Vienna.

Prov. Saskatchewan, Dept. Mineral Resources, Ind. Minerals Research Branch. Rep. Invest. Province of Saskatchewan, Department of Mineral Resources, Industry and Minerals Research Branch. Report of Investigation. Saskatchewan. Canada.

Przeglad Chem. Przeglad Chemiczny. Lemberg, Poland.

Przeglad Górniczy. (Mining Review). Warsaw.

Przeglad Papier. Przeglad Papierniczy (Paper Review). Lodz, Poland.

Przeglad Skórzany. (Leather Industry Review). Lodz, Poland.

Przem. Chem. Przemysl Chemiczny (Chemical Industry). Warsaw.

Pub. Astron. Soc. Pacific. Publications of the Astronomical Society of the Pacific. San Francisco, Calif.

Pub. Dominion Astrophys. Observatory, Victoria, B.C. Publications of the Dominion Astrophysical Observatory, Victoria, B.C., Ottawa.

Pub. Faculté Sci. Univ. Masaryk. Publications de la Faculté des Sciences de l'Université Masaryk. Moraira, Czech.

Pub. Health News. Public Health News. Washington.

Pub. Inst. Belge Amélioration Betterave. Publications de l'Institut Belge pour l'Amélioration de la Betterave. Tirlemont, Belgium.

Pub. Inst. Invest. Microquim., Unic. Nacl. Litoral. Publicaciones del instituto de investigaciones microquimicas, Universidad Nacional del Litoral. Rosario, Argentina.

Pub. Inst. Quim. 'Alonso Barba'. Publicaciones del instituto de quimica 'Alonso Barba'. Madrid.

Pub. Inst. Rech. Sidérurgie. Publications de l'Institut de Recherches de la Sidérurgie. Saint-Germain-en-Laye, France.

Pub. Sci. Tech. Ministère Air. Publications Scientifiques et Techniques du Ministère de l'Air. (France). Paris.

Publ. Carnegie Inst. Washington. Carnegie Institute of Washington. Publications. Washington.

Publ. Mass. Inst. Technol. Publications from the Massachusetts Institute of Technology. Boston.

Public Roads. Washington, D.C.

Public Works. New York.

Pulp and Paper. San Francisco.

Pulp Paper Mag. Can. Pulp and Paper Magazine of Canada. Gardenvale, Canada.

Q.J. Geol. Soc. The Quarterly Journal of the Geological Society of London.

Quart. J. Chem. Soc. Quarterly Journal of the Chemical Society. London.

Quart. J. Expt. Physiol. Quarterly Journal of Experimental Physiology. London.

Quart. J. Indian Chem. Soc. Quarterly Journal of the Indian Chemical Society. Calcutta.
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Quart. J. Math. Quarterly Journal of Mathematics. Oxford.
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Svensk Kem. Tid. Svensk Kemisk Tidskrift. Stockholm.

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Tec. Ital. Tecnica Italiana. Trieste.
Tech. Chem. Papier u. Zellstoff Fabr. Das Papier, Zeitschrift für die Erzeugung von Holzstoff, Zellstoff, Papier und Pappe. Darmstadt.
Tech. Eau. La Technique de l'Eau et de l'Assainissement. Brussels.
Tech. Mitt. Krupp. Technische Mitteilungen Krupp. Essen.
Tech. Moderne. La Technique Moderne. Paris.
Tech. Sanit. et Municip. Technique Sanitaire et Municipale. Paris.
Tech. Wiss. Abhandl. Osram-Konz. Technisch-wissentshaftliche Abhandlungen des Osram Konzerns.
Techn. Ind. Schweiz. Chem. Ztg. Technik und Industrie und Schweizer Chemiker Zeitung. Zürich.
Techn. Phys. U.S.S.R. Technical Physics of the U.S.S.R. Leningrad.
Techn. Rep. Osaka Univ. Technology Reports of the Osaka University. Osaka.
Techn. Rep. Tôhoku Imp. Univ. Technical Reports of the Tôhoku Imperial University. Tokyo.
Technique Moderne. Paris.
Technol. Quart. The Technology Quarterly and Proceedings of the Society of Arts. Massachusetts Institute of Technology. Boston.
Teer u. Bitumen. Teer und Bitumen. Halle.
Tehnički Pregled. Zagreb.
Teintex. Paris.
Tek. Fören. Finland Föhr. Tekniska Föreningens i Finland. Förhandlingar. Helsinki.
Tek. Tid. Uppl. C. Teknisk Tidskrift. Upplaga C. Stockholm.
Tekn. Tidskr. (Kem. Mekanik). Teknisk Tidskrift utgiven av Svenska Teknologföreningen. Upplaga Kemi, Mekanik. Stockholm, Norrköping.
Tekn. Tidsskr. Den Tekniske Forenings Tidsskrift. Stockholm.
Tekn. Ukeblad. Teknisk Ukeblad. Oslo.
Tekstil. Prom. Tekstil'naya Promyshlennost. Moscow.
Tekstil-Rundschau. St. Gallen, Switzerland.
Tellus. Tellus. Stockholm.
Teploenerg. (Thermal Power Engineering) Teploenergetica. U.S.S.R.
Termotecnica. Milan.
Tetsu to Hagane. (Journal of the Iron & Steel Institute). Japan.
Texas Agr. Expt. Sta. Bull. Texas Agricultural Experiment Station, Bulletin. College Station, Tex.
Texas Repts. Biol. and Med. Texas Reports on Biology and Medicine. Galveston, Tex.
Textil-Praxis. Stuttgart.
Textile Bull. Textile Bulletin. Charlotte, N.C.
Textile Colorist. New York.
Textile Mfr. Textile Manufacturer. Manchester.
Textile Rec. Textile Recorder. Manchester.
Textile Res. Textile Research. Princeton, N.J.
Textile Res. J. Textile Research Journal. Lancaster, Pa.
Textile World. New York.
Thonindustr. Ztg. (See *Tonindustr. Ztg.*).
Tids. Kjemi. Bergvesen. Tidsskrift för Kjemi og Bergvesen. Oslo.
Tids. Kjemi, Bergvesen Met. Tidsskrift för Kjemi og Bergvesen og Metallurgi. Oslo.
Tidsskr. Hermetikind. Tidsskrift för Hermetikindustri. Stavanger, Norway.
Tidsskr. Phys. Chem. Tidsskrift för Physik og Chemi. Copenhagen.

Timberman. The Timberman. Portland, Oregon.
Titanium Abs. Bull. Titanium Abstracts Bulletin. Washington.
Tohoku J. Exptl. Med. Tohoku Journal of Experimental Medicine. Tokyo.
Tonindustr. Ztg. Tonindustrie Zeitung. Wilhelmshaven.
Tonindustr. Ztg. u. Keram. Rundschau. Tonindustrie-Zeitung und Keramische Rundschau. Wilhelmshaven.
Toyo Rayon Shuho. Otsu, Japan.
Trans. Amer. Assoc. Cereal Chemists. Transactions of the American Association of Cereal Chemists. St. Paul, Minn.
Trans. Amer. Ceram. Soc. American Ceramic Society. Transactions. Columbus, Ohio.
Trans. Amer. Electrochem. Soc. Transactions of the American Electrochemical Society. New York.
Trans. Amer. Foundrymen's Assoc. Transactions, American Foundrymen's Association. Chicago, Ill.
Trans. Amer. Geophys. Union. National Research Council. American Geophysical Union. Transactions. Washington.
Trans. Amer. Inst. Chem. Eng. Transactions of the American Institute of Chemical Engineers. New York.
Trans. Amer. Inst. Elec. Eng. Transactions of the American Institute of Electrical Engineers. New York.
Trans. Amer. Inst. Metals. Transactions of the American Institute of Metals. Buffalo.
Trans. Amer. Inst. Min. Met. Eng. Transactions of the American Institute of Mining and Metallurgical Engineers. New York.
Trans. Amer. Inst. Min. Met. Eng., Inst. Met. Div. Transactions of the American Institute of Mining and Metallurgical Engineers. Institute of Metals Division. New York.
Trans. Amer. Microscop. Soc. Transactions of the American Microscopical Society. Columbus, Ohio.
Trans. Amer. Phil. Soc. Transactions of the American Philosophical Society. Philadelphia.
Trans. Amer. Soc. Civil Eng. Transactions of the American Society of Civil Engineers. New York.
Trans. Amer. Soc. Mech. Eng. Transactions of the American Society of Mechanical Engineers. New York.
Trans. Amer. Soc. Metals. Transactions of the American Society for Metals. Cleveland, Ohio.
Trans. Amer. Soc. Steel Treating. Transactions of the American Society for Steel Treating. Cleveland, Ohio.
Trans. Bose Inst. Res. Calcutta. Transactions of the Bose Research Institute. Calcutta.
Trans. Brit. Ceram. Soc. British Ceramic Society. Transactions. Stoke-on-Trent.
Trans. Butlerov Inst. Chem. Tech. Kazan. Transactions of the Butlerov Institute for Chemical Technology of Kazan. Omsk. U.S.S.R.
Trans. Cambr. Phil. Soc. Transactions of the Cambridge Philosophical Society. Cambridge.
Trans. Canad. Inst. Min. Met. Transactions of the Canadian Institute of Mining and Metallurgy and of the Mining Society of Nova Scotia. Quebec.
Trans. Canad. Inst. Min. Met. Eng. Transactions of the Canadian Institute of Mining and Metallurgy and Engineering. Quebec.
Trans. Ceram. Soc. Transactions of the British Ceramic Society. Stoke-on-Trent.
Trans. Chalmers Univ. Techn. Transactions of the Chalmers University of Technology. Gothenburg.
Trans. Connect. Acad. Transactions of the Connecticut Academy of Arts and Sciences. New Haven.
Trans. Dokuchaev Soil Inst. (U.S.S.R.). Transactions of Dokuchaev Soil Institute. Moscow.
Trans Edin. Geol. Soc. Transactions of the Edinburgh Geological Society. Edinburgh.
Trans. Electrochem. Soc. Transactions of the Electrochemical Society. Baltimore.
Trans. Faraday Soc. Transactions of the Faraday Society. London.
Trans. Geol. Soc. Edinburgh. (See *Trans. Edin. Geol. Soc.*).
Trans. Geol. Soc. S. Africa. Transactions of the Geological Society of South Africa. Johannesburg.
Trans. Illinois State Acad. Sci. Transactions of the Illinois State Academy of Science. Springfield, Ill.
Trans. Illum. Eng. Soc. Transactions of the Illuminating Engineering Society. Baltimore.
Trans. Indian Ceram. Soc. Transactions of the Indian Ceramic Society. Benares.
Trans. Inst. Appl. Chem. U.S.S.R. Transactions of the Institute for Applied Chemistry U.S.S.R. Moscow.

Trans. Inst. Chem. Charkov Univ. Charkov University, Transactions of the Institute of Chemistry.
Trans. Inst. Chem. Eng. Transactions of the Institution of Chemical Engineers. London.
Trans. Inst. Chem. Reagents, Moscow. Transactions of the Institution for Chemical Reagents, Moscow.
Trans. Inst. Chem. Tech. Ivanova. Transactions of the Institute for Chemical Technology of Ivanova (U.S.S.R.). Moscow.
Trans. Inst. Min. Eng. Transactions of the Institution of Mining Engineers. London.
Trans. Inst. Min. Met. Transactions of the Institution of Mining and Metallurgy. London.
Trans. Inst. Plastics Ind. Transactions of the Institute of the Plastics Industry. London.
Trans. Inst. Pure Chem. Reagents. Transactions of the Institute of Pure Chemical Reagents. Moscow.
Trans. Inst. Rubber Ind. Transactions of the Institution of the Rubber Industry. London.
Trans. Intern. Congr. Soil Sci. 4th Congr. Transactions of the International Congress of Soil Science. 4th Congress. Amsterdam.
Trans. Kansas Acad. Sci. Transactions of the Kansas Academy of Science. Lawrence, Kan.
Trans. Karpov Inst. Chem. Transactions of the Karpov Chemical Institute.
Trans. Kentucky Acad. Sci. Transactions of the Kentucky Academy of Science. Louisville.
Trans. IV Mendeleev Congr. Transactions of the Mendeleev Congress of Theoretical and Applied Chemistry. 4th Congress, Kharkov.
Trans. VI Mendeleev Congr. Theoret. Appl. Chem. Transactions of the 6th. Mendeleev Congress of Theoretical and Applied Chemistry. Kharkov. 1932.
Trans. Met. Soc. A.I.M.E. Transactions, American Institute of Mining, Metallurgical and Petroleum Engineers. New York.
Trans. Nat. Inst. Sci. India. Transactions of the National Institute of Sciences of India. Bangalore.
Trans. Opt. Inst. Leningrad. Transactions of the Optical Institute in Leningrad. Leningrad.
Trans. Opt. Soc. Transactions of the Optical Society. London.
Trans. Proc. New Zealand Inst. Transactions and Proceedings of the New Zealand Institute. Wellington, N.Z., London.
Trans. Proc. Roy. Soc. New Zealand. Transactions and Proceedings of the Royal Society of New Zealand. Wellington, N.Z., London.
Trans. R. Inst. Appl. Chem. U.S.S.R. Transactions of the Institute of Applied Chemistry, U.S.S.R. Moscow.
Trans. Roy. Dublin Soc. Scientific Transactions of the Royal Dublin Society. Dublin.
Trans. Roy. Soc. Transactions of the Royal Society. London.
Trans. Roy. Soc. Canada. Transactions of the Royal Society of Canada. Toronto.
Trans. Roy. Soc. Edin. Transactions of the Royal Society of Edinburgh. Edinburgh.
Trans. Roy. Soc. S. Africa. Transactions of the Royal Society of South Africa. Cape Town.
Trans. Roy. Soc. S. Austr. Transactions of the Royal Society of South Australia. Adelaide.
Trans. Sci. Chem. Pharm. Inst. Moscow. Transactions of the Scientific Chemical-Pharmaceutical Institute U.S.S.R. Moscow.
Trans. Sci. Inst. Fert. Insectofungicides U.S.S.R. Transactions of the Scientific Institute of Fertilizers and Insectofungicides. U.S.S.R.
Trans. Sci. Soc. China. Transactions of the Science Society of China. Taiwan.
Trans. Soc. Mech. Eng. Japan. Transactions of the Society of Mechanical Engineers. Tokyo.
Trans. State Inst. Appl. Chem. U.S.S.R. Transactions of the State Instititute for Applied Chemistry U.S.S.R. Moscow.
Trans. Wisconsin Acad. Sci. Transactions of the Wisconsin Academy of Science, Arts and Letters. Madison, Wis.
Trav. Congr. Jubilaire Mendeleev, Leningrad. Travaux du Congrès Jubilaire Mendeleev, Leningrad.
Trav. et Mém. Bur. Internat. Poids et Mes. Travaux et Mémoires du Bureau International des Poids et Mesures. Paris.
Trav. et Mém. Fac. Lille. Travaux et Mémoires de la Faculté des Sciences de l'Université. Lille.
Trav. Inst. Lomonossoff Géochim. Crist. Minéral. Travaux de l'Institut Lomonossoff de Géochemie, Cristallographie et Minéralogie. U.R.S.S. Moscow.
Trav. Inst. Métrol. Stand. U.R.S.S. Travaux de l'Institut de Métrologie et de Standardization de l'U.R.S.S. Moscow.
Trav. Lab. Biogéochim. Acad. Sci. U.R.S.S. Travaux du Laboratoire Biogéochimique de l'Académie des Sciences de l'U.R.S.S. Moscow.
Trav. Membres Soc. Chim. Biol. Travaux des Membres de la Société de Chimie Biologique.

Trav. Phys. Chim. Soc. Sci. Kharkoff. Travaux de la Section Physico-Chimique de la Société des Sciences Experimentales (à l'Université de Kharkoff). Kharkoff.

Trav. Soc. Pharm. Montpellier. Travaux de la Société de Pharmacie de Montpellier. France.

Trop. Agr. Ceylon. The Tropical Agriculturist. Ceylon.

Trop. Agr. (Trinidad). Tropical Agriculture. Trinidad.

Trudui Inst. Prom. Isuiskanii. Trudui Instituta Promyshlennost Isuiskaniĭ.

Trudy Arkhangel'skova Nauch. Issl. Inst. Trudy Arkhangel'skova Nauchno-Issledovatel'skovo Instituta.

Trudy Azer. Trudy Azerbaidzhanskovo Neftyanovo Issledovatel'skovo Instituta. Baku, Moscow.

Trudy Belorus. Sel'skokhoz. Akad. Trudy Belorusskoi Sel'skokhozyaistvennoi Akademii. Gorki, U.S.S.R.

Trudy Fiz.-Tekh. Inst. Akad. Nauk. U.S.S.R. Trudy Fiziko-Tekhnicheskovo Instituta, Akademiya Nauk Usbekskoi S.S.R. Moscow.

Trudy Gosudarst. Nauch-Issledovatel. i Proekt. Trudy Gosudarstvennovo Nauchno-Issledovatel'skovo i Proektnovo. Moscow.

Trudy Inst. Fiz. Khim. Akad. Nauk S.S.S.R. 2, Issledovaniya po Korozii Metal. Trudy Instituta Fizicheskoi Khimii, Akademiya Nauk S.S.S.R. 2, Issledovaniya po Korozii Metal. Moscow.

Trudy Inst. Fiziol. im. I. Beritashvili, Akad. Nauk Gruzin. S.S.R. Trudy Instituta Fiziologii imeni I. Beritashvili, Akademiya Nauk Gruzinskoĭ S.S.R. Tiflis.

Trudy Inst. Fiziol. Rastenii im. K. A. Timiryazeva, Akad. Nauk S.S.S.R. Trudy Instituta Fiziologii Rasteniĭ imeni K. A. Timiryazeva, Akademiya Nauk S.S.S.R. Moscow.

Trudy Inst. Khim. Akad. Nauk U.S.S.R. Trudy Instituta Khimii, Akademiya Nauk Uzbekskoi S.S.R. Moscow.

Trudy Inst. Khim. Akad. Nauk U.S.S.R. Inst. Khim. Trudy Instituta Khimii, Akademiya Nauk Uzbekskoi S.S.R., Instituta Khimii. Moscow.

Trudy Kharkov. Trudy Khar'kovskovo Khimiko-Tekhnologischeskovo Instituta im. S. M. Kirova. Kharkov.

Trudy Kharkov. Khim.-Tekhnol. Inst. im. G.M. Kirova. (See *Trudy Kharkov*). Trudy Kharkovskovo Khimii-Tekhnologii Instituta Imeni G.M. Kirova. Kharkov.

Trudy Khim. Inst., Kirgiz. Filial Akad. Nauk S.S.S.R. Trudy Khimicheskovo Instituta, Kirgizskii Filial Akademii Nauk S.S.S.R. Moscow.

Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R., Otdel. Khim. Nauk. Trudy Komissii po Analiticheskoi Khimii, Akademiya Nauk S.S.S.R., Otdelenie Khimicheskikh Nauk. Moscow.

Trudy Lab. Gidrogeol. Probl. Trudy Laboratorii Gidrogeologicheskikh Problem imeni Akademiya F.P. Savarenskovo, Akademiya Nauk S.S.S.R. Moscow.

Trudy Leningrad. Teknol. Inst. Trudy Leningradskovo Khimiko-Tekhnologicheskovo-Instituta. Leningrad.

Trudy Mineral. Muzeya, Akad. Nauk S.S.S.R. Trudy Mineralogicheskovo Muzeya, Akademii Nauk S.S.S.R. Moscow.

Trudy Moskov. Inst. Tonkoi Khim. Tekhnol. Trudy Moskovskovo Instituta Tonkoi Khimicheskoi Tekhnologii imeni M.V. Lomonosova. Moscow.

Trudy Moskov. Neftyan. Inst. Trudy Moskovskovo Neftyanovo Instituta imeni Akademii. I.M. Gubkina. Moscow.

Trudy Nauch.-Issledovatel. Inst. Khim., Khar'kov. Univ. Trudy Nauchno-Issledovatel'skovo Instituta Khimicheskovo, Kharkov University. Kharkov.

Trudy Sredneaziat. Trudy Sredneaziatskovo Gosudarstvennovo Universiteta. Tashkent U.S.S.R.

Trudy Sredneaziat. Univ. Khim. Nauk. Trudy Sredneaziatskovo Universiteta Khimicheskie Nauki. Uzbek S.S.R.

Trudy Ural. Ind. Inst. Kirova. Trudy Ural'skovo Industrial'novo Instituta imeni S.M. Kirova. U.S.S.R.

Trudy Vsesoyuz. Konf. Anal. Khim. Trudy Vsesoyuznoĭ Konferentsii po Analitcheskoĭ Khimii. Moscow, Leningrad.

Tschermak's Mineral. u. Petrog. Mitt. Tschermak's Mineralogische und Petrographische Mitteilungen. Vienna.

Tsement. Leningrad.

Tsvetnye Metal. (Non-ferrous Metals) Tsvetnye Metally. Moscow.

U.S. Atomic Energy Comm. United States Atomic Energy Commission. Washington.

U.S. Atomic Energy Comm. Nat. Sci. Found. Washington D.C. United States Atomic Energy Commission. Washington.

U.S. Bur. Fisheries Invest. Rept. United States Bureau of Fisheries, Investigational Report.

U.S. Bur. Mines Bull. Bureau of Mines Bulletin. Washington.
U.S. Bur. Mines, Inform. Circ. United States Bureau of Mines, Information Circulars. Washington.
U.S. Bur. Mines, Rep. Invest. United States Bureau of Mines, Report of Investigations. Washington.
U.S. Bur. Stand. J. Res. United States Bureau of Standards, Journal of Research. Washington.
U.S. Dept. Agr. Bull. United States Department of Agriculture Bulletin. Washington.
U.S. Dept. Agr. Circ. United States Department of Agriculture, Circulars. Washington.
U.S. Dept. Agric. Techn. Bull. United States Department of Agriculture. Technical Bulletin. Washington.
U.S. Geol. Survey Bull. United States Department of the Interior Geological Survey. Bulletin. Washington.
U.S. Geol. Survey Prof. Paper. United States Department of the Interior. Geological Survey. Professional Papers. Washington.
U.S. Nat. Bur. Stand. Circ. United States National Bureau of Standards. Circular. Washington.
U.S. Naval Med. Bull. United States Naval Medical Bulletin. Washington.
U.S.P. United States Patent.
U.S. Pub. Health Rep. United States Public Health Reports. Washington.
U.S.S.R. State Inst. Tobacco Invest. Bull. U.S.S.R. State Institute of Tobacco Investigation Bulletin. Moscow.
Uchen. Zapiski Beloruss. Univ. Uchenye Zapiski, Belorusskii Gosudarstvennyi Universitet imeni V.I. Lenina. U.S.S.R.
Uchen. Zapiski Kazan. Uchenye Zapiski, Kazanskiĭ Gosudarstvennyĭ Universitet imeni V.I. Ul'yanova-Lenina. Kazan, U.S.S.R.
Uchen. Zapiski, Leningrad. Uchenye Zapiski, Leningradskiĭ Gosudarstvennyĭ Pedagogicheskiĭ Institut imeni M.N. Pokrovskovo. Moscow.
Udobrenie i Urozhai (Fertilizers and Crops). Moscow.
Ukrain. Akad. Nauk Inst. Khim., Sbornik Trudov Pervoi Vsesoyuznoi Konferentzii (Neuprown) Rastvaram. Ukrainskii Akademii Nauk Institut Khimicheskii, Sbornik Trudov Pervoi Vsesoyuznoi Konferentzii (Neuprown) Rastvaram. Kiev. Ukr. S.S.R.
Ukrain. Chem. J. Ukrainian Chemical Journal. Kharkov.
Ukrain. Fiz. Zhur. Ukrains'kii Fizichnii Zhurnal. Kiev. Ukr. S.S.R.
Ukrain. Khem. Zhur. Ukrains'kii Khemichnii Zhurnal. Kharkov.
Ukrain. Khim. Zhur. Ukrains'kii Khimicheskii Zhurnal. Kiev. Ukr. S.S.R.
Umschau. Frankfurt a.M.
Underwriters' Labs. Inc., Bull. Res. Underwriters' Laboratories, Inc., Bulletin of Research. Chicago.
Union des Soc. Ind. France Troisième Congrès, Mulhouse. Union Internationale des Sociétés de Chimistes des Industries du Cuir, Troisième Congrès, Mulhouse.
Union S. Africa, Dept. Agr. Sci. Bull. Union of South Africa, Department of Agriculture, Science Bulletin. Pretoria.
Univ. Arizona Bull. University of Arizona Bulletin. Tucson.
Univ. Chile, Fac. Quim. y Farm., Tesis Quim. Farm. Universidad de Chile, Facultad de Quimica y Farmacia, Tesis de Quimicos Farmaceuticos. Santiago.
Univ. Florida Agr. Expt. Sta., Tech. Bull. University of Florida Agricultural Experiment Stations, Technical Bulletin. Gainesville, Fla.
Univ. Ill. Bull., Eng. Expt. Sta., Bull. Ser. University of Illinois Bulletin including Engineering Experiment Station, Bulletin Series. Urbana, Ill.
Univ. Mich. Stud. University of Michigan. Studies. Scientific Series. Ann Arbor.
Univ. Nebraska Stud. Studies of the University of Nebraska. Lincoln, Nebraska.
Univ. of Wash. Publ. in Fisheries. University of Washington Publications in Fisheries. Seattle.
Univ. Phil. Nat. Appl. Sci. Bull. University of the Philippines Natural and Applied Science. Bulletin. Quezon City, P.I.
Univ. Pittsburgh Bull. University of Pittsburgh Bulletin. Pittsburgh.
Univ. Studi Trieste, Fac. Sci., 1st. Chim. Università degli Studi di Trieste, Facoltâ di Scienze, Istituto di Chimica. Trieste.
Univ. Toronto Studies, Geol. Ser. University of Toronto. Studies. Geological Series. Toronto.
Univ. Toronto Studies, Pathol. Ser. University of Toronto Studies, Pathological Series. Toronto.
Univ. Wisc. Bull. Eng. Ser. University of Wisconsin. Bulletin. Engineering Series. Madison.
Univ. Wisconsin Agr. Expt. Sta., Res. Bull. University of Wisconsin Agricultural Experiment Station, Research Bulletin. Madison, Wis.

Uppsala Univ. Årsskrift. Uppsala Universitets Årsskrift. Uppsala.
Urol. Cutaneous Rev. Urologic and Cutaneous Review. West Palm Beach, Fla.
Uspek. Khim. Uspekhi Khimii. Moscow.
Uspekhi Fis. Nauk. Uspekhi Fisicheskikh Nauk. Moscow.
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Vacuum. London.
Veda Prirodui Praha. Prague.
Verhandl. Dritt. Komm. Intern. Bodenkundlich. Ges. Verhandlungen der dritten Kommission der Internationalen Bodenkundlichen Gesellschaft. Madison.
Verhandl. Schweiz. Naturforsch. Ges. Verhandlungen der Schweizerischen Naturforschenden Gesellschaft. Wabern-Bern, Switz.
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Verhl. K.K. Geol. Reichsanst. Wien. Verhandlungen der Königlich-Kaiserlichen Geologischen Reichsanstalt. Vienna.
Verhl. Naturhist.-Med. Vereins Heidelberg. Verhandlungen des Naturhistorischen-Medizinischen Vereins zu Heidelberg. Heidelberg.
Verhl. Opt. Inst. Leningrad. Verhandlungen des Optischen Instituts, Leningrad.
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Vestnik Akad. Nauk Kazakh. S.S.R. Vestnik Akademii Nauk Kazakhskoi S.S.R. Moscow.
Věstník Českoslov. Akad. Zemědělských věd. Věstník Československé Akademie Zemědělských věd. Prague.
Vestnik Inzhenerov i Tekh. Vestnik Inzhenerov i Tekhnikov. U.S.S.R.
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Vestnik Stát. Geol. Ust. Česk. Vestnik Státniho, Geologického Ustavu Československé Republiky. Prague.
Vestnik Ustred. Ustavu geol. Vestnik Ustredniho Ustavu Geologickeho. Prague.
Vestnik Ustredniho Jednoty Reparu Československcke. Prague.
Vestnik Venerol. i Dermatol. Vestnik Venerologii i Dermatologii. Moscow.
Vestsi Akad. Navuk Belarusk. S.S.R. Izvestiya Akademii Nauk Belorusskii S.S.R. Minsk, U.S.S.R.
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Vida Nueva. Havana, Cuba.
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Vierteljahresschr. Naturforsch. Ges. Zürich. Vierteljahresschrift der Naturforschenden Gesellschaft in Zürich. Zürich.
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Voy. Challenger Rep. Phys. Chem. Report on the Scientific Results of the Voyage of H.M.S. Challenger during the years 1873-6. London, 1880.
W. Virginia Eng. Expt. Sta. Tech. Bull. West Virginia Engineering Experiment Station, Technical Bulletin. Morgantown. West Virginia.
Wärme. Die Wärme. Düsseldorf.
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Waseda Appl. Chem. Soc. Bull. Waseda Applied Chemical Society Bulletin. Tokyo.
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Wasser u. Abwasser. Wasser und Abwasser. Berlin.
Wat. Wks. & Sewerage. Water Works and Sewerage. Chicago.
Wat. Wks. Eng. Water Works Engineering. New York.
Water & Sanit. Water and Sanitation. Toronto.
Water & Sewage. Water and Sewage. Toronto.
Water and Sewage Works. Chicago.
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Werkstoffe u. Korrosion. Werkstoffe und Korrosion. Weinheim, Germany.
West of Scot. Agr. Col. Ann. Rep. West of Scotland Agricultural College, Annual Report. Glasgow.
West Va. Univ. Tech. Bull. West Virginia University, Technical Bulletin. Morgantown, West Va.
Western Metals. Los Angeles.
Westinghouse Eng. Westinghouse Engineer. Pittsburg, Pa.
Wiadomości Chem. Wiadomości Chemiczne. Lodz, Poland.
Wiadsmosci Institut Metals and Metallography.
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Wien. Arch. Inn. Med. Wiener Archiv für innere Medizin und deren Grenzgebiete. Vienna.
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Wire Ind. Wire Industry. London.
Wis. Natuurkde. Tijdschr. Wis- en Natuurkundig Tijdschrift. Ghent.
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NITROGEN

SECTION I

THE OCCURRENCE, PREPARATION AND PRODUCTION OF NITROGEN

BY B. R. BROWN

THE OCCURRENCE OF NITROGEN

In the Atmosphere

CHEMICAL and geological arguments have been presented[1] which indicate the existence of layers of nitrogen, carbon dioxide, water and ammonia in the atmosphere during the early stages of evolution of the earth. Russell and Menzel[2] consider that the rate of escape of the permanent gases and of their cosmic distribution leads to the hypothesis that most, but not all, of the primitive nitrogen, argon and neon escaped rapidly during the initial cooling of the earth's surface. Urey[3] discusses the position of nitrogen in relation to the origin and development of the earth and other terrestrial planets and states that nitrogen in the form of ammonium salts or nitrides accumulated in condensed form at low temperature.

Investigations of the composition of the atmosphere have been made with V-2 rockets.[4–6] At altitudes up to 50 miles the atmosphere contains approximately 80 mol.-% of nitrogen and 19 mol.-% of oxygen.[4] Paneth *et al.*[5] state that at 70 km. the ratios of argon, helium and neon to the sum of nitrogen and argon are essentially the same as at ground level.

Kallman has shown by calculation that dissociation of nitrogen into atomic nitrogen occurs at an altitude of about 130–250 km.[6] Investigation of the auroral spectrum[7, 8] provides proof of the dissociation of nitrogen molecules in the upper atmosphere into neutral nitrogen atoms. The existence of onN_2^+ is in the ionosphere has been observed.[9–11] The formation of neutral nitrogen atoms and N_2^+ ions has been interpreted by Nicolet,[12] Deb,[13] Nicolet and Pastiels[14] and Regener.[15] Pelzer[16] rejected on thermodynamic grounds Vegard's assertion that solid nitrogen exists in the earth's atmosphere. It is reported[17] that the atmosphere of the earth forms a tail consisting of dissociated nitrogen, oxygen and hydrogen and having the shape of a conoid oriented with respect to the sun.

The origin of nitrous oxide in the atmosphere is attributed to reactions between nitrogen molecules and oxygen atoms formed by the photochemical dissociation of ozone.[18]

In the Sun

Biermann[19] states that nitrogen, carbon, oxygen, fluorine and neon together constitute approximately 34% of the composition of the sun, the most abundant element being hydrogen, which constitutes 55%, and helium (the second most abundant element) constituting 11%. Further investigations of the chemical composition are reported by Strömgren[20] and by Nicolet,[21] the former of whom reports that nitrogen is present in the sun to the extent of 300 atoms per million atoms of all kinds, or alternatively 0·4% by weight. These results are in qualitative agreement with the figures of Biermann and Strömgren.

In Stars, Nebulæ, Comets and Meteorites

Measurements have been made of the emission lines of many nebulæ and stars, and from these permitted and forbidden transitions of nitrogen, e.g. NII and NIII, have been identified.[22–29] Courtès[29] classified nebulæ into three groups on the basis of the variation in intensity of the forbidden NII lines at 6548–84 A. relative to H_α. Aller and Menzel[30] reported the abundances of various elements in the planetary nebulæ. The relative numbers of atoms are as follow: hydrogen 1,000, helium 100, carbon 0·6, oxygen 0·25, nitrogen 0·2, sulphur 0·036, neon 0·01, chlorine 0·002, argon 0·0015, and fluorine 0·0001; this composition is essentially the same as that of the sun. In a review of the rare gases Moureu[31] states that in crude nitrogen, from whatever natural source, there is an approximately constant proportionality between the constituent gases, except helium, which is irregularly distributed by virtue of local radioactive disintegration; this constancy suggests a common origin, i.e. in the pre-solar nebulæ. A critical discussion of the chemical composition of the stars has been presented by Gurevich.[32]

Spectra corresponding to the radicals NH and NH_2 have been observed[33] in the head and tail of the comet Encke. In a review[34] of the applications of photochemistry to astrophysics, Wurm states that excited molecules, such as N_2^+, with a long half-life, exist in the tails of comets.

In meteorites some elements such as nitrogen, carbon, oxygen, phosphorus, sulphur and selenium show low abundances as compared with abundances in the earth, sun and other celestial objects.[35] Estimates of 2–50 cu. mm. of nitrogen, hydrogen, carbon monoxide and carbon dioxide per gram of meteoritic iron have been made,[36] and the essential similarity of the gases in terrestrial and meteoritic steel was indicated.

In the Earth

A survey[37] of the abundances of elements in the ocean and sedimentary rocks as compared with their abundances in the weathered igneous rocks shows that nitrogen, carbon, oxygen (as water), chlorine, boron and bromine are highly concentrated in the surface materials. The presence of nitrogen in igneous rocks indicates that this element was present in condensed phases during the earth's formation (see also page 1). It has been calculated[38] that the lithosphere contains 0·004% of nitrogen by weight.

In a review[39] of the character of nitrogen and nitrate distribution, data have been presented which show that the accumulation of nitrate in Middle Asia is not due to the mineralization of organic residues from what were at one time centres of population; it is considered that nitrate deposits are the result of the processes of weathering of the earth's crust and of the nitrogen cycle in soils.

Plutonic rocks contain about 0·04 c.c. of nitrogen per gram; Rayleigh concluded from this fact that there is about 40 to 50 times as much nitrogen in rocks as is contained in the atmosphere.[40, 41]

The concentrations of nitrogen, helium and argon in the earth's crust decrease with increase in distance from the surface of the earth, in contradistinction to the concentrations of methane and carbon monoxide which increase.[42] Japanese workers have established[43] that the total nitrogen in phosphate rocks varies according to their mode of deposit and their geological age. The universal presence of nitrogen in uraninite has been discussed.[44] Khlopin and Coerling present data[45] on the ratio of helium and nitrogen of subterranean origin to that in the atmosphere, as well as the ratios of argon and nitrogen, which reinforce Moureau's hypothesis.[31] The composition of gases, including nitrogen, found in different rock strata and mines has been reported.[46–48]

The occurrence of elementary nitrogen, and of organic and inorganic nitrogenous compounds, in coal has been discussed.[49–58] Whilst proteins are not present in coal, it is generally agreed that the basic nitrogen structures are derived from animal and vegetable proteins and have not been greatly altered by the process of coalification.[51]

A possible mechanism is as follows: proteins are broken down by enzymes to give amino acids which in turn undergo condensation with aldehydes and hydroxy compounds present in carbohydrates to give relatively stable complex compounds. Free nitrogen and ammonia are derived from further breakdown of amino acids.

Considerable quantities of nitrogen occur in natural gases.[59–66] The composition of natural gas at Jirny, near Prague,[59] was 95·0% nitrogen, 3·2% carbon dioxide, 0·8% oxygen, 0·8% carbon monoxide and 0·2% unsaturated hydrocarbons. Nitrogen was found to be the main component in the gases at Tatar in Russia.[60] In the Donbass region[64] the gases in the coal formations consist of nitrogen, carbon dioxide, methane, helium, hydrogen and heavy hydrocarbons. At Daghestan[65] natural gas contains ca. 4% carbon dioxide, 0·7% methane, 0·5% hydrogen sulphide, 0·9% oxygen, 94·8% nitrogen and rare gases.

The nitrogen in natural gas was divided into three kinds by Belbusov[66] as regards its origin: (1) that produced as a result of biochemical processes in the upper zones of the lithosphere; (2) that produced by chemical processes at the higher temperatures in the earth's crust; and (3) atmospheric nitrogen.

Shale kerogen contains from 0·3% to more than 2% of nitrogen; indirect evidence is cited to show that the bulk of the nitrogen in shale kerogen is of protein origin.[67] Organic nitrogen compounds such as pyridine, pyrrole derivatives and nitriles have been identified in shale oil.[67, 68] A review of available data suggests that pyrrole homologues and porphyrin decomposition products in shale oil could be formed from the porphyrins (originating as chlorophyll) present in the kerogen. Pyrrole, indole, pyrocoll, pyridine-type bases, diazines, amides, nitriles and ammonia could also be formed from the protein matter in the kerogen.[67]

Nitrogen is among the elements found in petroleum[69, 70]; concentrations ranging from 0·013% (by weight) to 0·66% have been detected in various sources of petroleum. Katchenkov[69] considers that the distribution of elements can be explained only by a biogenic hypothesis of petroleum origin, since the occurrence of the various elements appears to be the same regardless of the location (U.S.S.R. and other countries).

In the Sea, Streams, Atmospheric Precipitation, etc.

In the waters of the Pacific Ocean,[71, 72] free ammonia is below 0·02 mg. per litre and decreases with depth; the albuminoid and organic nitrogen pass through minima of 0·02 and 0·05 mg. per litre respectively at about 800 metres depth and increase definitely again towards the sea bed. The average ratio of albuminoid to organic nitrogen was 0·57 for samples above 800 metres and 0·40 for samples below this depth.

In a review of the paleochemical and probable history of sea water, Rubey[73] states that the abundances of substances such as nitrogen, chlorine and water are similar to the relative amounts of the same materials escaping from hot springs and volcanoes; it is suggested that the hydrosphere and atmosphere may have come almost entirely from such plutonic gases.

The anomalous occurrence of fixed nitrogen in unpolluted surface and ground waters (e.g. 1·5–2·0 p.p.m. of nitrogen in mountain streams of Georgia, 2500 ft. above sea level) is believed due to leaching of soluble nitrogen compounds.[74]

The literature and data on the origin, chemical analysis and composition of atmospheric precipitation have been reviewed[75] comprehensively with respect to nitrogen with particular reference to the various forms in which it occurs in nature.

In Springs, Volcanoes and Geysers

The gas issuing from a thermal spring near Thabazimbi in the Transvaal was found to contain 99·6% of nitrogen plus inert gases.[76] In the same paper data are presented which show that gases from other springs contain large amounts of nitrogen. The origin of gases (including nitrogen) and trace elements found in the mineral springs of the Caucasian mineral waters has been discussed in relation to their formation in geological history.[77] The presence of nitrogen and other gases in the Sibukuro spring[78] has also been discussed with reference to their origin.

Nitrogen was detected spectroscopically in the burning gases of the Nyamuragira, Tshambene and Nyamlagira volcanoes during the eruptions of 1938–40.[79–81] Fresh incrustations in fumaroles of the 1937–38 eruption of the Klyuchevskoy volcano were mostly ammonium chloride, sodium chloride and potassium chloride.[82] Barth[83] states that gases reaching the surface of the earth are of two types, viz., volcanic gases (bearing hydrogen, hydrogen sulphide and carbon dioxide) and secondary gases (composed of nitrogen and oxygen). The geysers and hot springs of Iceland can be classified into those containing volcanic gases and those containing secondary gases. With increasing distance from magmatic sources the hydrogen, hydrogen sulphide and carbon dioxide contents fall until they become zero; the nitrogen and oxygen contents meanwhile increase.

The abundance ratio of the two nitrogen isotopes ^{14}N and ^{15}N from various natural sources is discussed in the section on atomic weight and isotopes (see page 137).

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THE FORMATION, LABORATORY PREPARATION AND PURIFICATION OF NITROGEN

Formation

Nitrogen is one of the gaseous products formed during the course of the reactions listed below, which have been investigated primarily for the study of reaction mechanisms:

Thermal decomposition of nitrites,[1–3] of guanidine chromate and dichromate,[4] of ammonium sulphate,[5] of hydrazine vapour on a silica surface[6] and of a potassium nitrate–charcoal mixture[7]; vapour phase reaction between hydrazine and oxygen[8]; photolysis of ammonia at 1849 Å.[9]; electric discharge decomposition of ammonia[10]; decomposition of ammonium salt solutions by exposure to light[11]; hypobromite and hypochlorite oxidation of ammonium hydroxide, hydrazine and hydroxylamine[12]; reaction of amino acids with nitrites[13]; reaction of concentrated nitric acid with iron containing carbon[14]; electrolysis of aqueous solutions of ammonium iodide.[15]

Laboratory Preparation

In their determination of some of the physical properties of nitrogen, Giauque and Clayton[16] prepared very pure nitrogen by the following technique. Gaseous ammonia was passed into bromine water, contained in a reaction vessel cooled in ice, so as to reduce the vapour pressure of bromine; the gas evolved passed through an ice-jacketed condenser to condense and return the bromine carried forward; the gas was then passed through a purifying train of potassium hydroxide sticks, anhydrous copper sulphate, 50% potassium hydroxide, concentrated sulphuric acid, solid potassium hydroxide and finally phosphorus pentoxide, all solutions used being first boiled under vacuum. The nitrogen so obtained was distilled three times; a small first fraction and the last quarter were rejected.

Harteck[17] obtained pure nitrogen by the catalytic decomposition of ammonia into nitrogen and hydrogen. Nickel powder heated to 1000°C. was used as a catalyst; ammonia was removed by freezing the gas in liquid air, and hydrogen was removed by solidifying the nitrogen and pumping off the impurity. The nitrogen obtained by this method contained 0·0015% of argon, 0·001% of oxygen and 0·0005% of a substance with a low saturation vapour pressure.

Bosworth[18] has described a convenient vacuum method for the preparation of nitrogen: a mixture of 2 parts of coarse potassium dichromate and 1 part of coarsely crushed ammonium sulphate (a slight excess over the stoicheiometric equivalent to ammonium dichromate) is heated in a tube; the evolution of nitrogen is controlled by the rate of heating and ceases when the heating stops. The nitrogen is purified by passage first through a liquid-air trap to remove water vapour and then over a tungsten filament at 2600°K., which removes oxygen and traces of nitrogen oxides. The thermal decomposition of ammonium dichromate is an explosive reaction, but the mixture of ammonium sulphate and ammonium dichromate is non-explosive probably because its reaction rate is controlled by a low collision frequency, owing to the slowness of diffusion in the solid state.

Rudenko,[19] also Smits and de Gruyter,[20] prepared and purified nitrogen by the conventional thermal decomposition of ammonium nitrite. The latter authors obtained the nitrogen by heating a mixture of sodium nitrite and ammonium sulphate in presence of potassium chromate and ammonium hydroxide. Purification was effected by scrubbing three times with potassium chromate in concentrated sulphuric acid, twice with concentrated aqueous sodium hydroxide and twice with concentrated sulphuric acid. After passage through a condenser cooled in liquid air, the gas was finally passed over heated copper; the last three stages of purification were then repeated.

Nitrogen prepared by the thermal decomposition of ammonium nitrite[21] and of sodium azide[22] was purified by repeated fractional distillation.

Purification

Most of the methods described below are concerned with the removal of oxygen from commercial nitrogen for laboratory purposes.

Oxygen can be removed by agitating nitrogen at 100 atmospheres for three hours in a steel bomb with a solution made from 25 c.c. of saturated ammonium carbonate solution, 25 c.c. of concentrated ammonium hydroxide, 50 c.c. of water and 10 g. of ammonium chloride, with small quantities of metallic copper and tin. Analysis by Hand's method shows that about 0·0001% of oxygen remains.[23]

By adapting an analytical method for the determination of small quantities of oxygen in gaseous mixtures, it is possible to obtain 1–2 litres of nitrogen per hour containing less than one part in $1{\cdot}7 \times 10^8$ of oxygen. In this method the gas is passed through a Gautier purifying bottle filled with fused white phosphorus, then through a Bender–Holbein bubbling apparatus containing 15% sodium hydroxide solution, and is finally scrubbed, in two similar containers, with saturated mercuric chloride solution.[24]

Water vapour and oxygen can be removed from nitrogen by passing the gas through a trap consisting of a large glass U tube containing a 25% sodium–75% potassium liquid alloy. As a means of drying the gas the sodium–potassium alloy trap compares favourably with silica gel and calcium chloride, but it is slightly less efficient than magnesium perchlorate; it has, however, the advantage of removing other impurities, the most important being oxygen.[25]

Kendall[26, 27] devised a new type of copper furnace for the removal of oxygen by the well-known copper–copper oxide method. The furnace contains a cylinder of copper gauze with a nichrome wire heater inside. With the heater at a temperature of 400–600°C. and a volume flow of 500 c.c./minute, the removal of oxygen is claimed to be complete. The copper oxide formed in the reaction is reduced by hydrogen to copper for further use. A further development of the Kendall furnace uses a Calrod heating unit[28] and another modification of this method uses copper turnings packed in an electrically heated iron pipe.[29]

By passing nitrogen containing about 0·08% of oxygen through a column of cobaltous oxide, the oxygen can be removed; it is important that the oxide be prepared in a high vacuum at a comparatively low temperature. Analysis by Hand's method shows complete absence of oxygen.[30]

A method of removing volatile metalloid compounds by treatment with halogens has been suggested.[31] Roedder described the purification of nitrogen by passage through sulphuric acid, activated alumina, magnesium perchlorate and finally over heated steel wool; this treatment removes carbon dioxide, carbon monoxide, water and oxygen.[32]

The separation of nitrogen from various gas mixtures has been carried out also by several physical methods. Barrer[33] reports the separation of nitrogen from argon–nitrogen and hydrogen–nitrogen mixtures using zeolite molecular sieves. The purification of nitrogen by glow discharge,[34] by thermal diffusion[35–37] and by using magnesium, calcium and barium as 'getters' has been reported.[38]

THE MANUFACTURE OF NITROGEN

It is relevant, before describing the manufacture of nitrogen, to discuss 'nitrogen fixation' and the so-called 'nitrogen industry'.

By nitrogen fixation is meant all those processes in which nitrogen in some combined form is returned to the soil for use in life processes. Nitrogen is essential to life, but neither animals nor the majority of plants can utilize it directly from the air. Broadly speaking the fixation of nitrogen falls into two categories, natural processes and man-made processes. Natural processes form part of the so-called 'nitrogen cycle' in which atmospheric nitrogen, converted into oxides of nitrogen by electrical discharge, is washed down by rain, nitric acid being formed in the process; in addition, some micro-organisms in the soil are able to assimilate elementary nitrogen.

Products formed by the micro-organisms are further used by plants, and in turn by animals for development, growth and the very process of living. The nitrogen is eventually returned to the soil by animal and vegetable decay and animal excreta. The methods used by man for the fixation of nitrogen include the following processes: (1) the direct synthesis of ammonia from its elements and, in connection with this, the production of nitric acid by oxidation of ammonia; (2) the formation of calcium cyanamide by the interaction of calcium carbide and nitrogen; and (3) the direct oxidation of atmospheric nitrogen. These processes together with the industries based on the use of Chile saltpetre are usually termed the 'chemical nitrogen' industries.

All these methods for the fixation of nitrogen are discussed in detail under the relevant headings; fixation by oxidative discharge is discussed under oxides of nitrogen; and methods for the production of ammonia, either direct or via cyanide, are given in the section on ammonia (see pages 241, 259).

Reviews on various aspects of nitrogen fixation have been presented by Hirschkind[39] and by Mittasch,[40, 41] who also discusses the agricultural uses of fixed nitrogen; Virtanen[42] has written an authoritative treatise on the nitrogen fixation cycle; Peckolt *et al.*[42] have discussed the fixation of atmospheric nitrogen by lightning; Dhar *et al.*[44] have reviewed the mechanism and efficiencies of biological and non-biological fixation. (Biological aspects of nitrogen activity are described in some detail on page 567.) Production and utilization figures for fixed nitrogen in several countries are reported,[45–50] and there are other reviews of general interest.[51–68]

World Production

World production figures prior to 1939 and up to 1959 for the chemical nitrogen industries are presented in Tables I and II.[69–74, 214]

Table I.—World Production of Chemical Nitrogen
(in thousands of short tons)

Type of Production	1900	1913	1924	1929	1934	1939
By-product	110·0	312·5	352·3	496·6	393·6	—
Ammonia and Arc		24·2	355·5	1102·1	1331·9	—
Cyanamide		42·0	120·5	250·7	238·5	—
Chilean Nitrate	220·0	472·7	412·4	554·8	144·5	250
TOTAL	330·0	851·4	1240·7	2404·2	2108·5	3160

Table II.—Production of Chemical Nitrogen by Countries
(in thousands of short tons)

Producing Country	1913	1924	1929	1934	1939	1947/48	1951/52	1955/56	1958/59
Germany*	131·6	470·7	889·9	462·5	1050			1020	1490
Chile	476·7	413·3	556·0	141·7	250	310	310	272	220
United States	39·5	129·6	318·9	256·7	350	1370	1750	3000	3440
Great Britain	99·5	108·4	217·7	175·0	166	356	496	505	615
France	18·9	33·6	103·9	187·5		188	290	486	696
Japan	3·9	36·9	90·5	208·0	500	232	510	796	1050
Norway	22·0	25·0	75·0	65·5		99	188	210	278
Italy	6·3	15·8	56·0	98·6		88	221	382	615
Belgium	10·9	13·9	44·2	109·8					
Netherlands	1·6	7·9	13·5	62·9					
U.S.S.R.	3·2	0·7	5·3	45·0					
All other countries	29·3	65·6	181·3	158·8					
Total	843·4	1321·4	2552	1972	2316	2643	3765	6671	8404

* From 1955—West Germany only.

Although nitrogen is not so important an industrial gas as oxygen, very considerable amounts of nitrogen are produced from the atmosphere. Comparable statistics for the production of elementary nitrogen do not appear to be available, except for U.S.A. whose production figures are quoted in Table III.[75, 76]

Table III.—United States Annual Production of Nitrogen (Compressed and Liquefied)

Year	Production of Nitrogen gas (million cu. ft.)
1950	1350
1951	2146
1952	2019
1953	2309
1954	2573
1955	3740

There are three main methods of manufacturing nitrogen, viz:

(*a*) low-temperature separation from air;
(*b*) removal of oxygen from air by combustion with a fuel;
(*c*) cracking ammonia.

Low Temperature Separation from Air

Nitrogen is produced in either the gaseous or the liquid state, and the same broad division exists as with oxygen: for large demands, gas producing plants are operated at or near the point of usage; for smaller demands, it is produced as liquid in central stations and shipped in tankers to customers for vaporization as required, or on the smallest scale it is supplied as compressed gas in cylinders.

Air is normally regarded as a binary mixture of oxygen and nitrogen, but there are also present appreciable amounts of water vapour, argon, carbon dioxide and small quantities of the rare gases neon, helium, krypton and xenon, together with traces of a number of other substances such as hydrogen, acetylene, ozone, carbon monoxide and nitrous oxide. It is essential, therefore, in all low temperature processes for the separation of oxygen and nitrogen, to remove from the air being processed any easily condensable constituents, such as water vapour and carbon dioxide, which would otherwise freeze and quickly block up the plant. The effect on the separation process of the other constituents, in particular argon (which has a boiling point between those of oxygen and nitrogen), must also be considered. Table IV indicates the concentrations and boiling points of the main constituents of the

Table IV.—Concentration and Boiling Points of the Constituents of the Atmosphere

Constituent	Concentration in dry air by volume	Boiling Point at 1 atm., °K.
Nitrogen	78·08%	77·35
Oxygen	20·95%	90·18
Argon	0·932%	87·29
Carbon dioxide	0·03%*	194·70 (sublimation temperature)
Neon	18·2 p.p.m.	27·15
Helium	5·24 ,,	4·22
Krypton	1·14 ,,	121
Xenon	0·086 ,,	165
Hydrogen	< 1·0 ,,	20·4
Hydrocarbons	< 1·0 ,, *	—

* This figure can be higher in heavily industrialized areas

atmosphere,[76] which may also contain variable traces of carbon monoxide, sulphur dioxide, nitrous oxide, ozone, nitrogen dioxide, ammonia, hydrogen sulphide and organic compounds, depending on local conditions.

Basically, all low-temperature separation processes for producing oxygen and nitrogen involve three operations: purification, in which the easily condensable gases such as water and carbon dioxide are removed, liquefaction and rectification.

PURIFICATION OF AIR

In the purification much of the moisture is removed by compression, and treatment of the compressed air with activated alumina removes a substantial fraction of that remaining. In some cases refrigeration-drying is used for the final drying of the air feed. Carbon dioxide is removed by scrubbing with sodium hydroxide solution or by a suitable absorbent such as soda lime, and in practice this is done between the compression and the final drying. In tonnage plants using regenerators instead of heat exchangers much of the residual moisture and carbon dioxide are deposited in the regenerators.

LIQUEFACTION

The compressed and purified air is then partially liquefied by splitting the air into two streams and expanding one stream either through an orifice (Joule–Thomson expansion, an isenthalpic process) or in an expansion engine (an isentropic process). In small plants where maximum efficiency is not the first essential, Joule–Thomson expansion only is used. Some of the 'cold' from the products is recovered by means of a heat exchanger in which the gaseous products pass countercurrent to the compressed air.

RECTIFICATION

Different cycles are used in the recovery of nitrogen from air depending on whether a plant is specifically operated to obtain pure nitrogen or is intended to produce pure nitrogen at the same time as pure oxygen. Plant design is further affected by the desirability of obtaining gaseous or liquid products.

Rectification of the partially liquefied air is performed in a single or double fractionating column. Where pure oxygen production is the primary consideration the nitrogen fraction obtained contains about 3% of oxygen in double-column plants and 8–11% of oxygen in single-column plants. The basic layout of a conventional oxygen–nitrogen plant with a double column is given in Fig. 1.

This type of plant is normally used in the manufacture of liquid oxygen. The nitrogen obtained at the same time is not usually sufficiently pure for most industrial purposes: it is therefore essential that the nitrogen be further purified, although some special plants are so operated that the products are pure nitrogen and impure oxygen.

It is relevant to mention here that the so-called 'tonnage' oxygen plants can also be adapted to produce a pure nitrogen fraction if required. These plants, usually constructed for the supply of gaseous oxygen to steelworks, are based on cycles different from the so-called 'Heylandt' cycle used in liquid oxygen plants. Liquid and gaseous oxygen plants will be discussed in greater detail under oxygen. Further information on tonnage oxygen plants can, however, be found in the review by Gardner.[76]

Where *liquid* nitrogen is the only pure product required, the arrangement shown in Fig. 2 is used. After compression and purification, the air is cooled by heat exchange with effluent-enriched air; it is then expanded and rectified in a single column. Pure liquid nitrogen and a waste gas-enriched air containing 27% of oxygen are obtained.

Where *gaseous* nitrogen is the only pure product required, the arrangement shown in Fig. 3 is operated. Prior to development of the double column system, a single-column process was used for the production of nitrogen gas.[79] The yield is relatively low as a consequence of the reflux requirements of the column. By the use of the

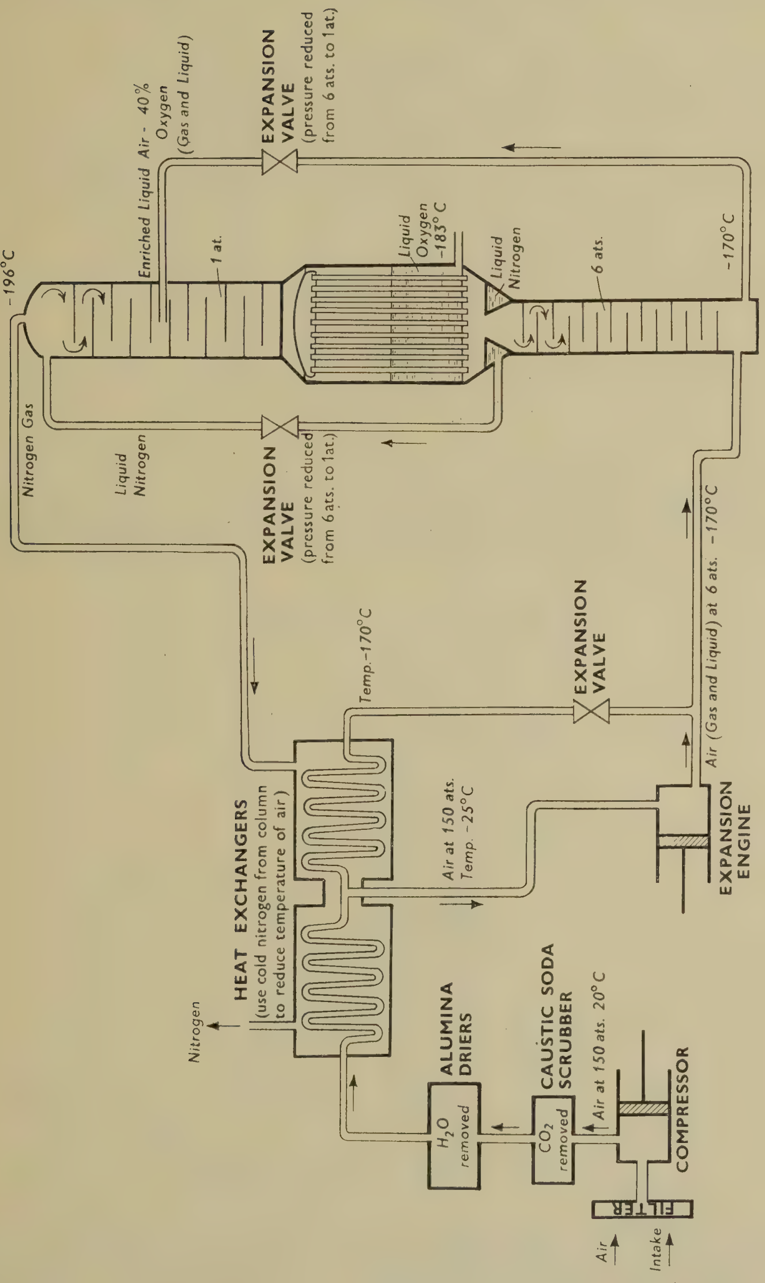
-196°C
Nitrogen Gas
Enriched Liquid Air - 40% Oxygen (Gas and Liquid)
1 at.
EXPANSION VALVE (pressure reduced from 6 ats. to 1 at.)
Liquid Oxygen -183° C
Liquid Nitrogen
6 ats.
-170°C
Liquid Nitrogen
EXPANSION VALVE (pressure reduced from 6 ats. to 1 at.)
Temp. -170°C
EXPANSION VALVE
Air (Gas and Liquid) at 6 ats. -170°C
HEAT EXCHANGERS (use cold nitrogen from column to reduce temperature of air)
Air at 150 ats. Temp. -25°C
EXPANSION ENGINE
Nitrogen
ALUMINA DRIERS
H_2O removed
CAUSTIC SODA SCRUBBER
CO_2 removed
Air at 150 ats. 20°C
COMPRESSOR
FILTER
Air
Intake

FIG. 1.—Conventional air separation plant (liquid oxygen production)

double-column system, rectification is improved and a high yield of nitrogen becomes possible. The lower column corresponds to the single column in Fig. 2, but the nitrogen fraction in the liquid from the sump is now almost completely removed in an additional column above the condenser. The liquid nitrogen from the lower column provides reflux for the top section of the upper column and strips oxygen from the vapour rising through that section. The vapour leaving the top tray has approximately the same composition as the entering liquid nitrogen and is withdrawn as product after heat exchange. Almost all the argon, amounting to 0·93% of the inlet air, leaves the column in the oxygen fraction which for this reason cannot contain more than 95·7% of oxygen. Because of the higher oxygen content, the condenser operates at a higher temperature than in a single column; the lower column pressure must therefore be increased to 75 instead of 45 lb./sq. in. absolute (for the single-column process). Plants of this type normally produce an oxygen fraction containing 92% of oxygen and a pure nitrogen fraction containing 10 to 100 p.p.m. by volume of oxygen, the yield of oxygen being about 98–99%.

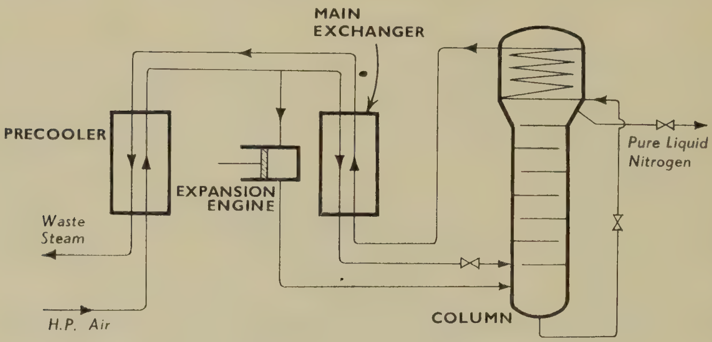

FIG. 2.—Pure liquid nitrogen from a single column

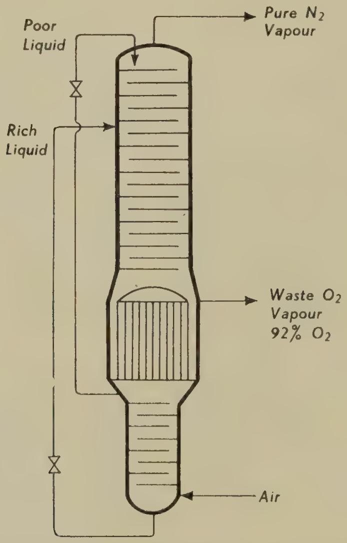

FIG. 3.—Pure N_2 gas from double column

Refs. p. 22

As will be seen later the double-column systems also allow the production of a small fraction of the nitrogen as liquid.

It is not possible to produce pure nitrogen and pure oxygen simultaneously by

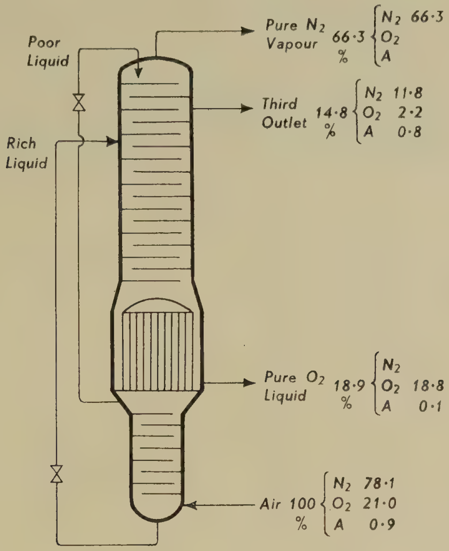

FIG. 4.—Pure N_2 and pure O_2 from double column

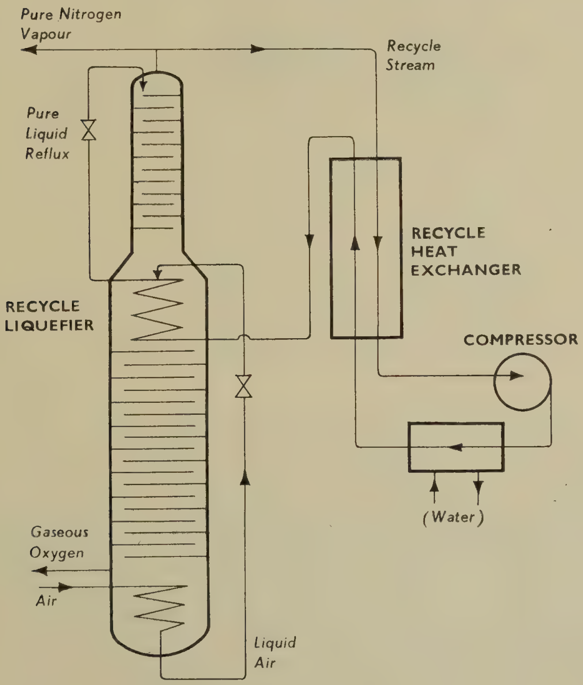

FIG. 5.—Pure nitrogen by recycle process

the conventional double-column system previously described, but this can be achieved by a simple modification,[80] whereby some of the vapour is removed from an intermediate point in the upper section (Fig. 4), which in effect increases the reflux ratio in this part of the column. With this higher reflux ratio the separation efficiency is increased, and by careful adjustment of the vapour taken from the 'third outlet' pure nitrogen is obtained. It is reported that with only 4% of the total air as third outlet, 90% oxygen recovery could be achieved at 99% purity and 98% recovery of nitrogen containing less than 10 p.p.m. of oxygen. Should the oxygen be required as liquid, the less favourable reflux conditions require that about 15% of the air must be removed as third outlet gas, assuming similar purities are to be achieved. The oxygen and nitrogen recoveries would then be about 90% and 85% respectively. For the successful operation of the third outlet system a high-purity liquid nitrogen reflux stream is required in the top column and this is provided by the lower column. If, instead of the double column, a single column is used, the reflux liquid is liquid air and the oxygen content of the nitrogen fraction will be at least 7%. The recovery of pure nitrogen from this stream requires a subsidiary process[81] as shown in Fig. 5. In this modification an extension is provided to the main rectification column in which part of the nitrogen fraction is further rectified to the required purity. To achieve this purity it is necessary to provide pure liquid nitrogen as reflux liquid. This is accomplished by taking part of the vapour from the product stream which, after warming, compressing and recooling, is liquefied by heat exchange with reflux liquid from the bottom of the additional column; the expanded liquid is then returned to the top of the subsidiary column.

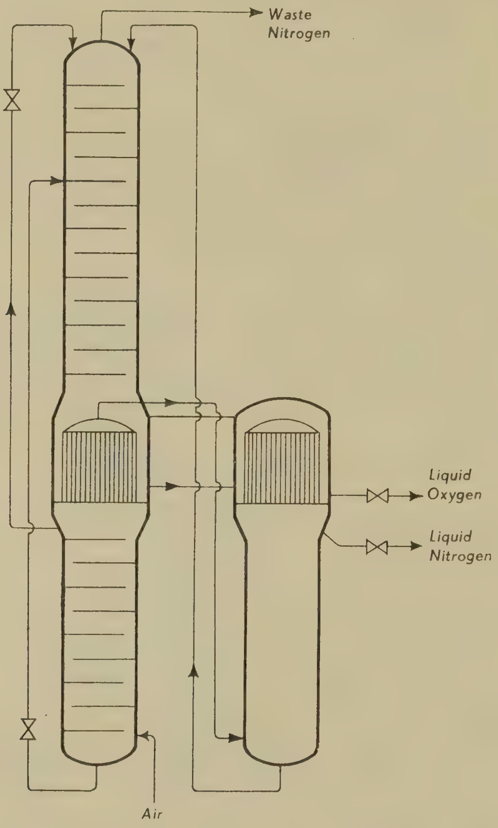

FIG. 6.—Pure N_2 side column

With the normal double-column system, the lower column is designed to produce a liquid nitrogen fraction ('poor liquid') containing about 2% of oxygen, and if this stream is restricted, thus increasing the lower column reflux ratio, a high purity liquid stream can be obtained. This method is used only for supplying minor quantities of pure liquid nitrogen because the double effect of restricting flow rate and withdrawing appreciable quantities of the poor liquid stream is to starve the upper column of reflux liquid which raises the oxygen content of the waste nitrogen stream and thus reduces the oxygen yield. This difficulty can, however, be surmounted either by providing extra trays in the lower column or by adding a side column as in Fig. 6. The side column condenser shell communicates with the main condenser shell and both are cooled by liquid oxygen. As can be seen from the diagram the lower column and side column act virtually as one column with an intermediate condenser an and intermediate withdrawal point for poor liquid.

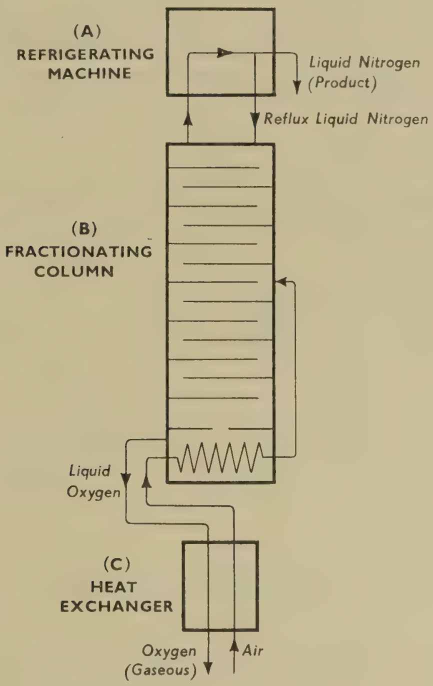

FIG. 7.—'Philips' liquid nitrogen producer

SMALL-SCALE PRODUCTION

A small apparatus designed to produce small quantities of liquid nitrogen in 1½ hours from 'start-up' has been invented[86]; the production rate is some 4–5 litres per hour. Fig. 7 shows the basic arrangement of the apparatus. In the heat exchanger C the air feed is partially pre-cooled by heat exchange with oxygen vapour coming from the column B; some of the moisture in the air is removed at the same time. The air is further cooled (and carbon dioxide and the remaining water vapour are removed), by heat exchange with liquid oxygen at the bottom of the fractionating column; at the same time this heat exchange results in vaporization of oxygen, some of which is removed via the heat exchanger. At some suitable point in this column (which contains metal gauze packings) the cooled CO_2-free, dry air enters. Fractionation of the air in the column gives virtually pure nitrogen at the top and on leaving the column this nitrogen is condensed in the refrigerating machine A. Some of the liquid nitrogen is returned to the column to provide the necessary reflux, and the remainder is removed as product.

The initial cooling of the apparatus to liquid air temperature is achieved by feeding the air supply directly to the refrigerating machine after removing water and carbon dioxide in a suitable trap; the liquid air thus produced is then passed to the column where it produces cooling by vaporization.

Many of the applications for 'pure' nitrogen can tolerate oxygen concentrations appreciably greater than 0·05%, e.g. for blanketing fuel tanks or foodstuffs during canning. In most cases, however, the nitrogen quality required is above that of the normal air separation unit waste gas, and a production method such as the third outlet scheme is necessary.

For the bright annealing of steel plates large quantities of dry gaseous nitrogen are required, practically free from oxygen (say less than 1 p.p.m.) and containing a few per cent. of hydrogen to give it reducing properties. These requirements can be met by adding excess of hydrogen to the crude nitrogen with subsequent catalytic removal of the oxygen. Fundamentally the initial oxygen content of the nitrogen is unimportant; therefore this method can be used for the further purification of 'pure' nitrogen, waste nitrogen from a conventional oxygen plant or even air itself. Other general industrial methods of purification of nitrogen from any source are discussed under 'Purification'.

STORAGE AND DISTRIBUTION OF LIQUID NITROGEN

Liquid nitrogen is stored in tanks completely surrounded by insulants such as basic magnesium carbonate, expanded mineral powders, e.g. 'Brelite' or 'Perlite' and slag wool; the whole is contained in an outer steel shell. Spherical and cylindrical tanks, which can hold quantities of up to 80 tons, are used; with good insulation an evaporation loss of as little as 0·6% per day can be achieved. For some applications and in particular for smaller tanks for special purposes where a specially low rate of loss is desirable, powder–vacuum insulation has been developed. In this device the tank is insulated by a double shell filled with a suitable fine powder which is evacuated to a pressure of the order of 0·1 mm. of mercury. By this means heat transfer by gas conduction is greatly reduced and radiation transfer largely suppressed.

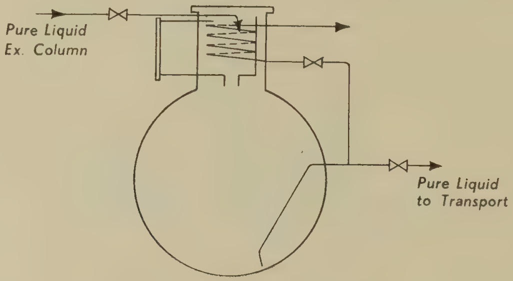

FIG. 8.—Pure liquid nitrogen storage

It is essential in the handling of pure liquid nitrogen to preserve the extremely high purity of the product and to reduce vaporization losses to a minimum. As a general rule liquid nitrogen is produced at a higher pressure than is economic for storage and transport and pressure release can cause a vaporization of up to 15%. This can be reduced considerably by undercooling the liquid before reducing the pressure. Alternatively, liquid nitrogen can be stored at a pressure exceeding 1·7 atm., i.e. at a boiling point exceeding the dew-point of the atmosphere, whereby rapid heat transfer to the liquid nitrogen from the condensed air on the walls of the storage vessel is prevented. As nitrogen is more volatile than oxygen, gradual evaporation of the liquid by heat influx into the storage tank leads to an accumulation of oxygen in the liquid phase. By using the device shown in Fig. 8,[77] this undesirable effect is eliminated. The vapour which would normally escape from the tank is condensed on the outer surface of the coil situated in the vapour space, by allowing an equivalent quantity of the liquid to expand to atmospheric pressure through this coil. The storage pressure may thus be held constant and the vaporization loss transferred entirely to the relatively oxygen-rich phase which safeguards the purity of the stored product.

A general description of equipment techniques used in storing and handling liquefied gases is given in papers by Davis[82] and Eastland.[83]

In addition to the papers by Gardner[76] and Littlewood and Shuftan[77] on air separation and the production of nitrogen, the reader is referred to the general works on the principles and practice of the separation of gases by Davies[84] and Ruhemann.[85]

Removal of Oxygen from Air by Combustion. Nitrogen Generators

Where quantities of nitrogen are required for processes of an intermittent nature the so-called nitrogen generators are useful. The basis of this method is the combustion of a fuel (gas, liquid or solid) with air, the ratio of fuel and air being so adjusted that the oxygen content is completely removed.[87–90] Water vapour and carbon dioxide are also removed if necessary.

The Holmes–Kemp nitrogen generators,[87] (see Fig. 9), produce a high-quality inert gas by the controlled combustion of fuel gas and fuel oil. Capacities of plant available range from 1000 to 50,000 cu. ft. per hour. Oil-fired generators use gas oil or diesel oil as a fuel and the majority of gas-fired generators utilize town gas. Some plants do, however, use fuel gases such as propane, butane, hydrogen, producer gas or water gas. In all types the fuel is burned under pressure with the exact amount of air required for combustion in a horizontal water-jacketed combustion chamber which is usually firebrick lined. The hot inert gas is then cooled, leaving the generator at a pressure designed to suit the application, normally of the order of 1 lb./sq. in. above atmospheric pressure and at a temperature within a few degrees of that of the available cooling water. Table V gives typical analyses of the inert gas produced from the two types of generator using town gas or oil as fuel.

Table V.—Composition of Gas produced by Nitrogen Generators

	Town-gas Fired	Oil Fired
Carbon dioxide	12%	15%
Nitrogen	87%	84%
Oxygen	less than 1%	less than 1%
Carbon monoxide	less than 1%	less than 1%
Oxides of nitrogen	0·0075% approx.	0·015% approx.
Sulphur dioxide	Equivalent to approx. 20% of the original sulphur in the fuel	

Substantially pure nitrogen can be obtained by the removal of carbon dioxide. Counter-current scrubbing in a packed tower with monoethanolamine removes carbon dioxide and other acidic gases. Regeneration of the amine is done by pumping the carbonated amine solution from the bottom of the absorber to the top of a stripping tower via a heat exchanger which raises its temperature: as the solution passes down the packed bed of the stripper, it meets rising vapour generated in the reboiler and attains a temperature high enough to liberate the carbon dioxide.

The removal of oxides of nitrogen can be accomplished by subjecting the impure nitrogen gas to a pressure of not less than 180 lb./sq. in. above atmospheric pressure for a period sufficient to oxidize the nitric oxide to nitrogen dioxide, and by subsequent washing of the combustion gases to remove nitrogen dioxide.[91]

A variation of this process has been described in which[92] air is passed through a copper coil heated to about 500°C., when the oxygen is removed as copper oxide, and then a gaseous fuel is passed through the coil to reduce the oxide. It is stated that one gallon of gasoline furnishes 3000–5000 cu. ft. of nitrogen.

The inert gas leaves the generator fully saturated with water vapour and for certain applications it is desirable to dry the gas to sub-zero dew-points. Conventional desiccants such as silica gel or activated alumina are used, reactivation of the adsorbent being carried out by means of steam coil or electric heaters.

Related to this process is the method of obtaining nitrogen for use in a heat-treating furnace by forcing hot furnace gas successively through heated retorts containing iron chips and charcoal and then through the furnace and back through the retorts.[93]

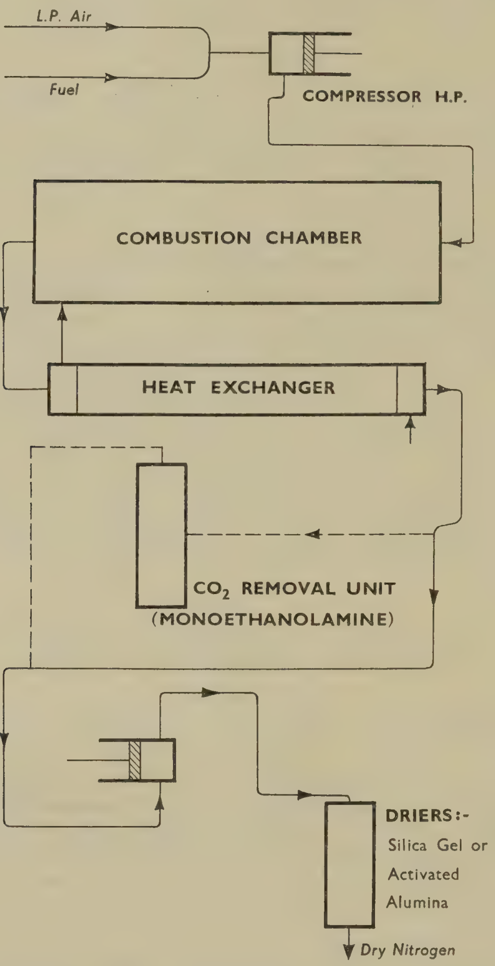

FIG. 9.—Flow diagram for Holmes–Kemp nitrogen generators

The production of pure nitrogen or nitrogen–hydrogen mixtures may be achieved[94, 95] by the combustion of hydrogen–air mixtures on an incandescent refractory bed the temperature of which is maintained by the heat of combustion. It is claimed[94] that explosion hazards are eliminated and that at the maximum output of 500 l./hr. the oxygen contents before and after purification are respectively 0·15% and 0·01%.

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The reaction between a heated fuel, steam and air has been utilized for the production of nitrogen–hydrogen mixtures.[96, 97]

Natural gas and petroleum deposits usually contain substantial quantities of nitrogen. Natural gas provides a very convenient fuel in the nitrogen generator method; the nitrogen already present in the gas increases the yield normally obtained from the air.[98]

The separation of nitrogen from coke-oven gases is important only in connection with the production of hydrogen for ammonia synthesis or for purification of the gas for fuel purposes. Liquefaction and fractional distillation processes such as the Linde–Bronn method are normally used.[99–108]

By passing coke-oven gases over iron oxides heated to about 750°C. and then passing the resultant gases continuously through a mass of coke heated to about 1200°C.,[109] a gas containing hydrogen, carbon monoxide and a small quantity of nitrogen is obtained.

The greatest use of nitrogen in industry is for the production of ammonia. All the processes previously described can be used for this purpose. Methods of producing 'synthesis gas' (i.e. a mixture of $1N_2:3H_2$) are discussed in the section on ammonia production (see page 259).

Cracking of Ammonia

The dissociation or 'cracking' of anhydrous ammonia, which is one of the cheapest and purest of the heavy chemicals, provides another very convenient source of nitrogen, in particular where it is also desirable to have present a reducing agent such as hydrogen. Although ammonia is synthesized from nitrogen and hydrogen in the first place, it can be cracked directly into its component elements by reversing the conditions required for its synthesis. At temperatures of about 600°C. and at pressures from below atmospheric to about 15 atm., ammonia in the presence of a catalyst is almost completely decomposed into nitrogen and hydrogen.[110] Ammonia is quite easily liquefied by compression and hence can be readily transported to the operation site where it is dissociated by catalytic methods discussed below. In some cases the nitrogen–hydrogen mixture produced from the cracked ammonia is used directly,[111, 112] but because of the inflammability of the mixture it is usual to remove some or all of the hydrogen by combustion with air.

In a typical example of this process[113] a controlled mixture of 69% of air and 31% of ammonia at above 500°C. is passed over a platinized alumina catalyst and a rhodium catalyst supported on alumina. Cracking of the ammonia and combustion of the hydrogen with oxygen take place simultaneously, water vapour is removed partly by condensation and partly by conventional driers and the resulting mixture contains 80% of nitrogen and 20% of hydrogen. Oxides of nitrogen can be removed by scrubbing with liquid nitrogen; liquid oxides of nitrogen and substantially pure nitrogen are the end products.[114]

The catalysts employed in this process are usually metals of the platinum group; the so-called 'Nitroneal generators' use catalysts of platinum, palladium, rhodium and indium.[115] The oxides of iron, aluminium, magnesium, calcium, zirconium and chromium have been used in some cases[116–122]; these metal oxides and the oxides of nitrogen[123] are sometimes used merely for the combustion process after catalytic cracking.

Sometimes non-catalytic processes are used in which the cracking and combustion are performed in a wide flame,[124] or in a heated iron coil,[125] or by burning preheated air in an atmosphere of ammonia gas.[126–128]

Miscellaneous Processes

Other processes for manufacturing nitrogen which are of only minor importance, or have merely been suggested, are described below.

Nitrogen produced by chemical reactions, such as the thermal decomposition of ammonium nitrite, finds application in some industries.[129–131]

The separation of nitrogen from various gas mixtures by adsorption with conventional adsorbents has attracted some attention.[132–137] In one example of techniques[132] of this type, air is cooled by direct contact with the cooled adsorbent, by refrigeration or by heat interchange with cold-product streams and then passes up through a downward flowing fluid bed of granular adsorbent. Activated charcoal, activated bauxite, activated alumina or silica gel is used. The mass rate of flow of adsorbent downwardly through the separation zone and the mass rate of feed gas introduced are adjusted so that the total heat capacity of the flowing granular adsorbent approximates to that of the gaseous mixture to be separated. The desorption of the more readily adsorbable constituents is brought about by heating a fraction of one of the gas products and subjecting further quantities of the rich adsorbent to direct contact with the heated gas. A charcoal circulation of 37 tons/hour serves to separate 2×10^6 cu. ft./day of high-purity oxygen and 8×10^6 cu. ft./day of nitrogen. In normal operation a small proportion, between 5% and 15% by weight, of the charcoal flow is removed and subjected to high-temperature reactivation.

The separation of nitrogen from oxygen and other gas mixtures by centrifugation has been proposed.[138–141] From theoretical considerations, Khariton[142] concludes that the process is not efficient. The separation of gases by permeation of plastic membranes is not at present considered to be of economic importance.[143] Diffusion has been considered as a possible method for the separation of nitrogen–hydrogen mixtures.[144, 145] The reaction between hæmoglobin and oxygen to form oxyhæmoglobin has been suggested as a basis for separating the oxygen and nitrogen of the air, the hæmoglobin being recovered by subjecting the oxyhæmoglobin to reduced pressure.[146]

Schemes for the recovery of nitrogen from rotary lime kilns have been described.[147]

A nitrogen generator for some types of aircraft utilizes energy derived from its normal operation to obtain a continuous flow of nitrogen by absorption of the oxygen from cooled compressed air with a cobalt compound.[148]

Purification for Industrial Purposes

Oxygen is removed from nitrogen by passing the gas over uranium nitride $UN_{(1\cdot5-1\cdot75)}$ at 500–600°C. The uranium nitride is prepared by passing nitrogen or ammonia over uranium turnings at about 800°C.[149] A new apparatus using the heated copper method has been described.[150] Small proportions of oxygen or gases such as hydrogen sulphide can be removed by treatment with a molten metal such as lead or copper in the form of fine particles.[151] Several ways of removing oxygen by combustion with hydrogen in the presence of a catalyst have been suggested. Using alumina impregnated with 10% of silver at about 250°C. and a gas pressure of 2000 lb./sq. in., oxygen concentrations have been reduced to 0·001% and less.[152] Alternative catalysts are palladium, deposited on a support consisting of alumina or zinc oxide,[153] and carborundum.[154] Copper, in the form of pellets or finely divided metal or as a deposit on a suitable carrier such as alumina–silica gel, has been suggested, as also has a mixture of manganese oxides.[155] In these hydrogen combustion methods excess of hydrogen can be removed by liquefying the oxygen-free nitrogen when a gaseous residue of hydrogen is obtained.[156] An apparatus containing low-carbon steel discs heated to 800°C. has been used, the oxygen being fixed as oxides on the disc surfaces; for reactivation, the oxides are reduced with hydrogen.[157] The use of a solution containing sodium hyposulphite, $Na_2S_2O_4$, sodium hydroxide and sodium anthraquinone-β-sulphonate has been suggested for oxygen removal.[158]

Sulphur dioxide can be removed by extraction with various ethers and esters such as ethylene glycol monoacetate,[159] monoethanolamine, etc.

By passing nitrogen containing methane, carbon monoxide or carbon dioxide over finely divided aluminium heated to 700–950°C., these impurities may be removed[160]; the aluminium may be mixed with an inert material, e.g. aluminium silicate or oxide as a support.

Other ways of purifying nitrogen, which are normally used for the purification of nitrogen–hydrogen mixtures, include reaction with zinc or cadmium vapour for removing oxidizing impurities,[161] scrubbing with ammoniacal copper solution to remove carbon monoxide[162] and reaction with hopcalite to convert carbon monoxide to carbon dioxide.[163]

Pumice on which is deposited 7% of nickel and 3% of aluminium is a very active and stable catalyst for converting into water the last traces of oxygen in nitrogen–hydrogen mixtures.[164] Reduction by hydrogen at 500°C. in the presence of a catalyst of 2% of copper and 3% of nickel deposited on chamotte is also useful in eliminating oxygen.[165]

The methods for producing industrial nitrogen atmospheres and for purifying nitrogen for industrial processes have been reviewed.[166]

More details about nitrogen–hydrogen mixtures are given in the section on the manufacture of ammonia (see page 259).

THE USES OF NITROGEN

Ammonia and Cyanamide Production

The principal large-scale use of pure nitrogen is in the synthesis of ammonia from its elements. The hydrogen is usually obtained from organic sources by oxidation processes, and pure liquid nitrogen is sometimes used as a scrubbing medium for removing residual carbon monoxide[85, 167] from the crude hydrogen, as in the Linde–Bronn process, for example, or in the production of synthesis gas from refinery gases.[77, 85, 168, 169] Where the oxidation reaction is used the air separation unit is sometimes integrated with the ammonia plant,[168, 170] but in general pure nitrogen is used in synthesis only when pure hydrogen (such as electrolytic hydrogen or hydrogen separated from coke-oven gas[171]) is used. Thus processes in which hydrogen is obtained as water-gas by reducing steam with coke usually obtain nitrogen from producer gas. Details of the plant used in hydrogen production from refinery vent gas, using liquid nitrogen as a scrubbing medium, are given in a paper by Jester.[172]

Another major use is the production of calcium cyanamide from calcium carbide[173–175] (see page 240).

Metallurgical Operations

Pure nitrogen gas, produced by air separation or nitrogen generators or from cracked ammonia, has a further major use as an inert atmosphere for such operations as bright annealing steel,[77, 85, 168, 176, 181] distilling zinc from brass scrap,[182] general heat treatment of non-ferrous metals[171, 183] and preventing decarburization during the heat treatment of steel[171,184,185]; the introduction of small quantities of hydrogen into nitrogen also gives a safe reducing atmosphere for these operations.

Nitrogen finds application in other metallurgical operations, e.g. in nitriding and in the flushing of molten metals, particularly copper and aluminium alloys, to remove dissolved gases and so avoid porous castings.[186] Although nitrogen is used for degassing and removing oxides from metals such as zinc and lead, argon is more versatile and completely unreactive.[186–190] Nitrogen has been used in brazing and soldering ferrous and non-ferrous metals,[191] and in the refining of aluminium.[192]

Miscellaneous Uses

The use of nitrogen in the preservation of foodstuffs and in the canning industry, particularly in U.S.A., is becoming increasingly important.[186, 193, 194]

The demand for high-purity liquid nitrogen is small in relation to that for pure

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gaseous nitrogen[168]: in fact the liquid is produced mainly for convenience of storage and transport where a particular demand for the pure gas is insufficient to justify erection of an independent plant.

Liquid nitrogen, however, finds some direct application by virtue of its 'cold content', for example in shrink fitting.[168, 195] Recently the use of liquid nitrogen for 'superchilling' of foodstuffs for preservation during storage and transport has been described. In this application the foodstuff is packed in well-insulated containers and initially chilled by liquid nitrogen to about −150°F.[196] The subsequent temperature rise due to heat influx is slow and permits transit times of up to 40 days' duration without loss of effective refrigeration, thus avoiding the need for means of refrigeration during the transit period.[168, 196] Another recent use of liquid nitrogen is in the freeze-grinding of plastics and of foodstuffs[186,197]; in this process the plastic or foodstuff is made brittle with liquid nitrogen and can then be ground into powder.

Further uses of gaseous and liquid nitrogen of minor importance are: pressurized nitrogen in high-tension cables and high-voltage condensers[171, 186, 198–200]; the vulcanization of rubber[201–203]; flame extinction and prevention of explosions in mines[204–206]; the production of cyanides[207, 208]; the formation of aerosols[209]; the production of carbon black from hydrocarbons[210]; hardening stainless steel with liquid nitrogen[171] for low-temperature working; desulphurizing hydrocarbon oils[211]; refining petroleum oils[212]; and enamelling of iron.[213]

The uses of the ^{15}N isotope are discussed in the section on atomic weights and isotopes (see page 137).

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SECTION II

PHYSICAL PROPERTIES OF NITROGEN

BY B. R. BROWN

STRUCTURE

Solid Nitrogen

Solid nitrogen exists in two enantiotropic forms with a transition point of 35·61° ± 0·05°K. according to the determination of Giauque and Clayton.[1] Clusius[2] gave 35·4°K. for the transition point.

According to de Smedt, Keesom and Mooy,[3] α-nitrogen at 20°K. possesses either a cubic structure with the unit-cell dimension $a = 5{\cdot}656$ A. or a tetragonal structure with $a = 4{\cdot}00$ and $c = 5{\cdot}656$ A. Because the solid exhibits double refraction these authors believe that the structure is tetragonal, with four atoms to the unit cell. Vegard[4–7] found, however, that it possesses a face-centred cubic structure (space-group T^4) with a molecular lattice containing four molecules in the unit cell ($a = 5{\cdot}66$ A.); the distance between centres of molecules is 4·0 A. and the centre-to-centre distance between the two atoms in one molecule is 1·065 A. (see Fig. 1). This has been confirmed by Ruhemann[8] who also found a cubic structure with $a = 5{\cdot}67 \pm 0{\cdot}02$ A.

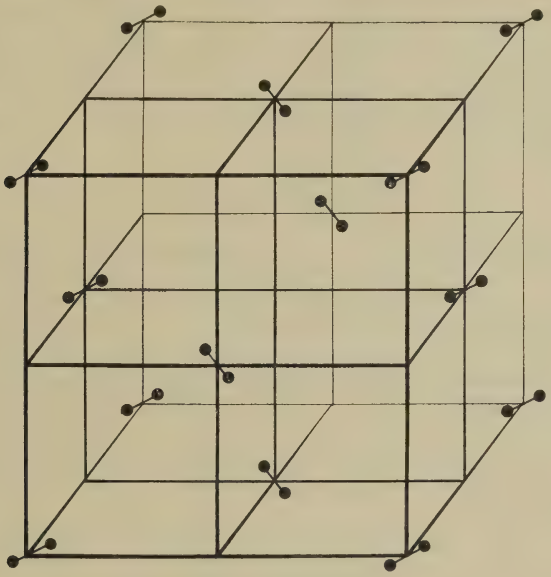


FIG. 1.—Crystal structure of α-nitrogen

According to Vegard[4] this structure is similar to that of sodium chlorate, $NaClO_3$, and is approximately one of closest spherical packing.

β-Nitrogen at 39°K. crystallizes in a hexagonal form of close sphere packing; the unit cell contains two molecules with $a = 4{\cdot}03_4 \pm 0{\cdot}009$ A. and $c/a = 1{\cdot}633$.[8] Vegard found a similar structure with $a = 4{\cdot}039$ A. and $c/a = 1{\cdot}691$.

On bombarding α-nitrogen with electrons a characteristic spectrum is emitted.[9] This has been interpreted by Vegard,[10, 11, 12] who believes that it is due to forbidden electronic transitions from metastable molecular states. β-Nitrogen, in contrast, does not display this phenomenon; the molecules in β-nitrogen can apparently rotate, and this precludes formation of metastable states and makes phosphorescence impossible. This investigation has been continued with mixtures of solid nitrogen and inert gases.[12, 13] From a general equation for non-polar face-centred cubic lattices London has calculated that the lattice energy of α-nitrogen is 1·64 kcal./mole.

The reader is also referred to the work on activated nitrogen molecules and atoms formed at low temperatures (about 4°K.); this is discussed in the section on active nitrogen.

Liquid Nitrogen

A monochromatic *X*-ray diffraction pattern for liquid nitrogen obtained by Sharrah[15] was analysed for atomic and electronic distributions. The distribution curve showed diatomic aggregates comparable with those found in the gaseous state. The structure of liquid nitrogen has also been investigated by Henshaw *et al.*,[16] who measured the scattering of neutrons of wave-length 1·08 A.; a single neighbour was found 1·1 A. from each atom, which corresponds to the presence of diatomic molecules in the liquid, in agreement with the work of Sharrah.

Further consideration of the structure of liquid nitrogen has been given from a theoretical standpoint[17–20]; some authors[17] point out that the *X*-ray scattering data obtained by Sharrah are inadequate for obtaining the atomic distribution curve. Structural investigations for the transition vapour to liquid[21, 22] indicate a picture of dynamic association of molecules rather than distinct macroscopic regions of inhomogeneity.

Ortho-Para Nitrogen

From the intensity changes in band and Raman spectra Justi[23] concluded that normal nitrogen consists of 2 parts of para-nitrogen with even rotational quantum numbers, and 1 part of ortho-nitrogen with odd rotational quantum numbers. The existence of ortho–para states for nitrogen had previously been forecast by Bonhoeffer and Harteck.[24] Justi[23, 25] claims to have prepared pure para-nitrogen starting from solid nitrogen, the evidence for the existence of para-nitrogen resting solely on a difference in vapour pressures. Later workers[26, 27] were unable to confirm this result. According to Smits and de Gruyter[26] the deviation in the results obtained can be explained if the vapour pressure difference is extremely small and also if, in the separation of para- from ortho-nitrogen, equilibrium of the normal mixture is very quickly attained.

"Metallic" Nitrogen

Horovitz[28] has shown from energy considerations that a metastable metallic form of nitrogen can exist; an approximate calculation of its properties has been made.

Comparison of Nitrogen and Carbon Monoxide Molecules

Vegard[29] pointed out the great similarity in a number of the physical and chemical properties of nitrogen and carbon monoxide. This is to be expected since the two molecules have the same number of extra-nuclear electrons. It is interesting, therefore, to compare the solid forms of the two substances.

α-Carbon monoxide and α-nitrogen have practically identical space groups, lattice dimensions, relative positions of molecules and distances between centres of atoms in the molecules. The dimensions of the unit cell are also similar (carbon monoxide, 5·63 A.; nitrogen, 5·66 A.).[29]

β-Carbon monoxide has a crystal structure almost identical with that of β-nitrogen. In both cases the molecules in the lattices rotate. The arrangement approximates very nearly to closest sphere packing. The axial ratios are: β-carbon monoxide $c/a = 1{\cdot}651$; β-nitrogen $c/a = 1{\cdot}633$; and for β-carbon monoxide $a = 4{\cdot}11$, while for β-nitrogen $a = 4{\cdot}039$.[30]

Many other similarities are mentioned later in this review.

DISSOCIATION

The dissociation constant of the reaction $N_2 \rightleftharpoons 2N$ has been calculated from spectroscopic data[1, 31] for the temperature range 298° to 20,000°K.; these results are presented in Table I.

Table I.—Dissociation Constant of Nitrogen

T°K.	$K_p = (N)^2/(N_2)$	Ref.	T°K.	K_p	Ref.
298·1	1×10^{-128}	1	5000	0·294	2
500	1×10^{-74}		6000	5·94	
1000	2×10^{-34}		7000	52·7	
2000	4×10^{-14}		8000	281	
3000	3×10^{-7}		9000	1064	
4000	7×10^{-4}		10,000	3165	
5000	8×10^{-2}		12,000	$17{\cdot}1 \times 10^3$	
			14,000	$58{\cdot}8 \times 10^3$	
			16,000	149×10^3	
			18,000	304×10^3	
			20,000	522×10^3	

Values of the free energy function

$$\left[\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right)\right]$$

for the dissociation of nitrogen have been estimated by Giauque and Clayton[1] for the temperature range 298°K. to 500°K.

Heat of Dissociation

Table II gives the values obtained, and the methods used in the determination of the heat of dissociation of nitrogen.

A reasonable value of the heat of dissociation from the above data would be 225 kcal./mole (≡9·764 ev.) which is in good agreement with the figure of 9·756 ev. adopted by the National Bureau of Standards.[80]

From consideration of calorimetric and spectrographic data the following heats of emission (or absorption) accompany the valency changes indicated.

$V^0 - V^{I} = 9{\cdot}2$ kcal.; $V^0 - V^{II} = 106{\cdot}9$ kcal.
$V^{II} - V^{IV} = 152{\cdot}7$ kcal.; $V^{I} - V^{III} = 172{\cdot}3$ kcal.
$V^{III} - V^{IV} = 159{\cdot}6$ kcal.[61]

A theoretical formula has been developed for the molecular dissociation of nitrogen in the upper atmosphere resulting from the action of the ultra-violet light of the sun.[62]

Table II.—Heat of Dissociation of Nitrogen

Ref.	Author	Year	Method	kcal./mole
32	Gaviola	1928	Spectroscopic data	226
33	Herzberg	1928	N_2^+ Band spectra	226
34	Birge & Mulliken		Calculation based on Herzberg's data[33]	219
35	Kaplan	1929	Dissociation of N_2^+	208
36	Bay & Steiner	1930	Active Nitrogen Studies and Hg vapour. Spectra	222
37	Stäckel	1930	Thermal interpretation of bonds	207
38	Datta	1932	Absorption spectrum of N_2O	203
39	Sutton	1932	Recalculation of Datta's data[38]	208
40, 41	Lozier	1933	Measurement of electron energy necessary to produce atomic ions	182·5
42	Herzberg & Sponer	1934	Spectroscopic data of Nitrogen	169·6
43	Hylleraas	1935	Calculation	169·6
44	Hemptinne & Savard	1935	Ionization potentials	155·2
45	Chakravorti	1938	Wave-mechanical calculation	168
46	Schmid & Gero	1943	Spectroscopic data	122·4
47	Schmid & Gero	1944	Spectroscopic data	115·3
48	Gaydon	1946	Birge–Sponer method	225
49	Glockler	1948	Bond energies	225
50	Hagstrum	1948	Electron impact & Band spectroscopy	170
51	Swarc	1949	Thermal decomposition of hydrazine	225
52	Glockler	1949	Bond Energies	225
53	Glockler	1950	Comparison with CO	272
54	Cario & Reinecke	1950	Calculation and Review	225
55	Kaplan	1950	Review	170
56, 57	Kistiakowsky, Knight & Malin	1951	Detonation velocity of C_2N_2–O_2 mixture	225
58	Thomas & Gaydon	1952	Spectroscopic study of C_2N_2–O_2 reaction	225
59	Farber & Darnell	1953	Dissociation of N_2 on tungsten filament	225
60	Pauling	1954	Bond Energies	170

DENSITY OF GASEOUS NITROGEN

Values of density of nitrogen in g. per litre at N.T.P. as determined by different workers are given in Table III.

Table III.—Density of Nitrogen at N.T.P.

Year	Authors	Density, g./litre	Ref.
1927	Moles & Clavera	1·2504 ±0·00003	63
1928	Baxter & Starkweather	1·25036	64
1934	Moles & Salazar	1·25049	65
1937	Moles	1·25046	66
1950	Moles	1·250525	67

The value used by the National Bureau of Standards, 1·25046 g./litre, (0°C., 1 atm.) is in fair agreement with the above results, but the most recent value 1·250525, obtained by Moles (1950) appears to be the most accurate. The Bureau also give the molecular weight of nitrogen as 28·016 g.-mole.$^{-1}$.

COMPRESSIBILITY

Experimental Data

The pressure and temperature ranges over which various workers have reported experimental *P–V–T* data are listed in Table IV.

Table IV.—Sources of Compressibility Data for Nitrogen

Year	Authors	Temperature Range, °C.	Approximate Pressure Range, atm.	Ref.
1928	Bartlett, Cupples & Tremearne	0 to 400	1 to 1000	68
1930	Bartlett, Hetherington, Kvalnes & Tremearne	20 to −70	1 to 1000	69
1930	Basset & Dupinay	16	1000 to 5000	70
1935	Bridgman	23·5 to −140 &−183 to −196	3000 to 6000	71
1934	Michels, Wouters & de Boer	0 to 150	20 to 85	72
1934	Otto, Michels & Wouters	0 to 150	45 to 416	73
1936	Michels, Wouters & de Boer	0 to 150	192 to 2960	74
1937	Benedict	0 to −183	100 to 1550	75
1937	Benedict	−175 to 200	1000 to 5840	76
1951	Tsiklis & Krichevskiĭ	50 to 150	6500 to 10,000	77, 78

According to Din,[79] at temperatures above 320°K., the data of Michels *et al.*[72–74] agree generally with those of Holborn and Otto (Mellor, VIII, 54). At pressures above 100 atm. the data of Bartlett[69] and Benedict[75, 76] agree reasonably well with each other and also with Michels' data extrapolated below 0°C. From 500 atm. to 700 atm. Benedict's data lack precision. At pressures from 4000 atm. to 6000 atm. Benedict's data are to be preferred to Bridgman's,[71] since in the region of 6500 to 10,000 atm. the data of Benedict and Tsiklis[77, 78] are in better agreement than those of Bridgman.[71] A selection of these data is given in Table V.

Tables of smoothed *P–V–T* data based on the experimental results listed above have been compiled by various authors; this information is discussed in the section on enthalpy, entropy and free energy (see page 45). Some of the smoothed values published by the National Bureau of Standards[80] in 1955 are given below. The method of obtaining these data and their reliability are discussed in a later paragraph. The results are expressed as the compressibility factor, $Z = PV/RT$.

°K.	0·01 atm.	1 atm.	10 atm.	100 atm.
100	0·99982	0·981	—	—
300	1·00000	0·99982	0·99838	1·0054
600	1·00000	1·00044	1·00439	1·0465
1000	1·00000	1·00036	1·00360	1·0365
3000	1·00000	1·00014	1·00135	1·0135

Some of the correlated *P–V–T* values calculated by Michels *et al.*[81, 82] (see page 46) which cover a wider pressure range than those of the National Bureau of Standards are given in Table VI. (The N.B.S. report that in the same range Michels' data agree with their data.)

Table V.—Compressibility of Nitrogen—Selected Values

Temp., °C.	Pressure Atm.	*PV* Amagat Units	Ref.
−70	1	0·7432	69
	100	0·6362	
	1000	1·7783	
−25	1	0·9090	69
	100	0·8676	
	1000	1·9600	
0	19·0215	0·99274	72
	192·30	1·03032	74
	1753·64	3·03129	74
150	30·0240	1·56697	72
	346·72	1·85767	74
	2960·95	5·11820	74
−183	99·90	0·16110	75
	399·73	0·59537	
	1252·00	1·6704	
−125	99·89	0·29979	75
	981	1·5527	
	1955	2·7346	
	5351	6·2776	
−75	1955	2·9518	76
	3413	4·5886	
	4866	6·0772	
	5835	7·0183	
0	2442	3·8432	76
	3413	4·9278	
	5835	7·4331	
100	2442	4·2737	76
	3413	5·3875	
	5835	7·9012	
200	2442	4·7161	76
	3413	5·8352	
	5835	8·3572	
50	6500	8·2680	77, 78
	7500	9·1800	
	8500	10·0810	
	10,000	11·4500	
100	6500	8·5475	77, 78
	7500	9·4950	
	8500	10·4040	
	10,000	11·7400	
150	6500	8·7815	77, 78
	7500	9·7275	
	8500	10·6420	
	10,000	12·020	
399·3	1	2·4621	68
	100	2·5729	
	400	2·9422	
	1000	3·7196	
299·8	1	2·0978	68
	100	2·1928	
	400	2·5498	
	800	3·0615	
198·9	1	1·7283	68
	100	1·8071	
	400	2·1407	
	1000	2·9165	

Table VI.—Compressibility of Nitrogen (Michels)

Pressure, atm.	−125°C.	−50°C.	0°C.	50°C.	100°C.	150°C.
0	0·5427	0·8174	1·00045	1·18358	1·36671	1·54985
1	0·5384	0·8162	1·00000	1·18357	1·36700	1·55036
10	0·5030	0·8052	0·99616	1·18166	1·36979	1·55510
50	0·3425	0·7654	0·98558	1·18829	1·38519	1·57847
100	0·2846	0·7448	0·98470	1·20443	1·41215	1·61358
200	0·4378	0·7862	1·03616	1·26904	1·48894	1·70074
600	1·0356	1·3160	1·52501	1·74068	1·95672	2·17101
1000	1·5727	1·8638	2·06756	2·27560	2·48584	2·69623
2000	2·7836	3·1139	3·33110	3·54444	3·75715	3·96947
4000	—	—	5·5963	5·83700	6·06996	6·30243
6000	—	—	7·682	7·938	8·19999	8·45688

PV values of Nitrogen in Amagat Units

Virial Coefficients

Values of the 2nd virial coefficient (B) in the equation

$$PV = RT\{1 + (B/V) + (C/V^2) + \dots\}$$

have also been obtained from measurements of the velocity of sound; these are given in Table VII.[83, 84]

Table VII.—Values of B for Nitrogen in the Equation $PV = RT\{1 + (B/V) + (C/V^2) + \dots\}$

Temperature	*B*, Amagat units	
°K.	Keesom *et al.*[83]	Van Itterbeek *et al.*[84]
70	−13·38	−13·68
80	−10·319	−10·65
90	−8·411	−8·61
100	−7·026	−7·12
110	−5·937	−5·97
120	−5·052	−5·06
130	−4·322	−4·33
140	−3·711	−3·72
150	−3·204	−3·21

The evaluation of the second, third and fourth virial coefficients from theoretical considerations, usually by means of the Lennard-Jones 6:12 intermolecular potential, has been reported.[85–97]

By means of a differential method a comparison has been made of the compressibilities of carbon monoxide, carbon dioxide, nitrous oxide, oxygen, ethylene and propane with nitrogen at pressures below 1 atm.[98] Whilst theory predicts that for compressible gases below their critical point there should be a slight curvature towards the pressure axis in the PV/P isothermals, in no case, even with propane, was any curvature in the isotherms detectable.

Constants in Equations of State

Jablczynski[99, 100] calculated the value of the constants in the van der Waals equation as applied to nitrogen. Coefficient b is a constant and has an average value $b = 0·310$; but coefficient a is not constant and changes with temperature and volume. Curves of a and b versus p, traced by Herman[101] in an investigation at

0°C. and $p=1-3000$ atm. showed, however, that both a and b decrease as p increases. The deviations are explained on the assumption of polymerization increasing with pressure. Making the further assumption that the van der Waals equation is valid for both the simple and polymerized molecules (with different constants), Herman was able to deduce a relation between the concentration of polymerized molecules (N_4) and the volume. At 1650 atm. $N_4=0{\cdot}38$ and at atmospheric pressure $2N_4/N$ is found to be 2×10^{-4} (N being the concentration of the unpolymerized molecules); the value deduced from coefficients of absorption is $1{\cdot}8-2{\cdot}3\times10^{-4}$.

Wohl[102] also discussed the calculation of the van der Waals constants a and b. Corrected values for a and b were calculated from equations deduced for the second virial coefficient taking into consideration the temperature coefficient of a and b.

A somewhat different method of determining the van der Waals constant has been given by Rundle.[103] He shows that the value of a calculated from the values of $\gamma(C_p/C_v)$ is in good agreement with the value calculated from critical data.

An attempt to account for certain of the physical properties of nitrogen, using the hypothesis of molecular aggregation, has been made by Keyes and Taylor.[103a]

The constants of the Beattie–Bridgman equation of state have been determined by Beattie and Bridgman[104, 105] for nitrogen and by Deming and Shupe[106, 107] for a $3H_2-1N_2$ mixture.

Corner[108] has shown that there is fair agreement with the constants a and b of the Beattie–Bridgman equation of state as determined by experiment and by calculation from the third virial coefficients as computed by de Boer and Michels. Using a two-constant intermolecular potential Corner calculated values for $a/B_0=0{\cdot}45$ and for $b/B_0=-0{\cdot}1$.

A comparison of nitrogen and oxygen according to the principle of corresponding states has been made by Nijhoff,[109] who found that oxygen and nitrogen do not correspond in their deviations from this law, contrary to the results reported by earlier workers.

Duclaux[110, 111] considers that if the compression of a gas is regarded as a progressive association, it should be revealed in the plot of $[P(V-b)/RT]$ versus $\log(V-b)$, in that all isotherms of the same gas can be superimposed by a simple transposition along the $(V-b)$ axis. This is verified for nitrogen (as well as for oxygen and argon) to temperatures within 3° of T_c and for pressures above $0{\cdot}8\ P_c$. As, however, there is no relation between the isotherms of different gases, Duclaux suggested that corresponding states do not exist. In a later paper[112] he states that oxygen and nitrogen have no strictly corresponding states, but within the limit of experimental error more or less extended zones of correspondence exist.

Wergeland[113] has presented a simple model for the approximate description of agglomeration of molecules in the gas phase. Using the method of Darwin and Fowler, the Gibbs phase integral is deduced, and hence an equation of state. Satisfactory agreement is found between theory and observation for nitrogen.

Guggenheim[114] states that application to nitrogen of the principle of corresponding states in virial coefficient form shows that nitrogen in the vapour or liquid state follows the principle fairly closely but that with solid nitrogen the agreement is not so good.

Cook and Rowlinson[115] also discussed the deviation of nitrogen from the principle of corresponding states as developed from intermolecular potentials which are functions of the orientation of the molecules.

Maron and Turnbull[116] derived a general equation for all gases from the Beattie–Bridgman equation in which the activity coefficient of the gas is given as a function of the reduced temperature and reduced pressure only. Activity coefficients for nitrogen calculated from their equation are compared with activity coefficients read from Newton's generalized curves at various reduced temperatures and pressures. At values of the reduced temperature and pressure, $T_r\geqslant1{\cdot}3$ and $P_r\leqslant12$, the agreement is within 4%, and for $T_r\geqslant1{\cdot}5$ with the same value of P_r the agreement is within 3%; at values of $T_r=1{\cdot}2$ or lower the agreement is not so good, but improves as the value of P_r is reduced.

Refs. p. 48

Further modification of the principle of corresponding states and its application to nitrogen has been considered.[117–119]

The Benedict–Webb–Rubin equation of state has been evaluated for nitrogen by Stotler and Benedict.[120]

A paper by Levitt[121] relates pressure and volume for nitrogen by the empirical equation $p = Ce^{B/V}$ (where B and C are constants); it is valid for nitrogen at high pressures and constant temperatures. Other empirical equations have been proposed: Linhart's[122] applies to nitrogen and a $3H_2:1N_2$ mixture over a wide pressure and temperature range; Milosavliévitch's[123] holds for nitrogen at and below the critical pressure; Daub's[124] holds for nitrogen at $-70°$, $0°$ and $100°$ and has the form $PV = AP^r - (P^2 + BP + C)^n$, where A, B, C, r and n are constants; Popoff's[125] having the form $PV = RT^{(1+\alpha)}$ is deduced starting from the Nernst Theorem.

DENSITY OF LIQUID AND SOLID NITROGEN

Liquid Nitrogen

Workers at the National Bureau of Standards[126] have recently reported density values for the liquid and the saturated vapour which are given in Table VIII. Liquid density was measured by observing the rise and fall of Pyrex glass floats, and vapour density was determined by calculation from ideal solution laws.

Table VIII.—Density of Liquid Nitrogen

T°K.	Liquid ρ g./c.c.	Vapour g./c.c.
70·38	0·8431	0·0019
71·40	0·8374	0·0023
73·91	0·8269	0·0028
76·21	0·8163	0·0039
77·68	0·8095	0·0045
80·23	0·7978	0·0059
80·32	0·7974	0·0059
82·57	0·7871	0·0073
84·35	0·7789	0·0085
88·10	0·7617	0·0116
89·38	0·7557	0·0128

Armstrong[127] has shown that the saturation vapour density (ρ, g./cm.^{3}) can be represented by the equation

$$\log \rho_T = 3{\cdot}39858 - \frac{282{\cdot}953}{T - 3{\cdot}83}$$

Solid Nitrogen

The density of the solid is given in Table IX.

Table IX.—Density of Solid Nitrogen

Temperature, °C.	α-Solid ρ g./cm.^{3}	β-Solid ρ g./cm^3	Authors	Year	Ref.
−210·02 (triple point)		0·956	Simon, Ruhemann & Edwards	1930	128, 129
−210·02		0·947	Keesom & Lisman	1934	130, 131
−228		0·982	Vegard	1934	30
−253	1·0265				

Refs. p. 48

Vegard's density values were determined from *X*-ray crystallographic data whilst the results of Simon *et al.* and of Keesom and Lisman were obtained from their experiments on the variation of melting point with pressure.

VAPOUR PRESSURE OF SOLID AND LIQUID NITROGEN

The ranges of temperature covered by various workers in their vapour pressure measurements are listed below in Table X with a selection of some of the values.

Table X.—Vapour Pressure of Solid and Liquid Nitrogen

Year	Authors	Temperature, °K.	Vapour Pressure	Ref.
1935	Aoyama & Kanda	α-Solid 34·69 β-Solid 62·52	0·0015 mm. 76·2 mm.	132, 133
1933	Giauque & Clayton	β-Solid 54·783 Triple point 63·136 Boiling point 77·32 Liquid 78·008	12·79 mm. 94·01 mm. 760† mm. 823·23 mm.	1
1937	Keesom & Bijl	β-Solid 53·264 Triple point 63·16 Boiling point 77·357 Liquid 77·59	8·225 mm. 94·01 mm. 760·0 mm.† 781·0 mm.	134
1941	Kirshenbaum	64·11 74·61	112·50 mm. 545·00 mm.	135, 139
1954	Armstrong	64·1776 Boiling point 77·364 77·6644	112·9 mm. 760·0 mm. 915·8 mm.	127
1950	Friedman & White	Boiling point 77·34 77·86 Critical 126·26	760·0 mm.* 1·0527 atm. 33·54 atm.	136, 137
1953	Michels, Wassenaar, de Graaf & Prins	96·853	6·1720	138

* Extrapolated. † Interpolated.

Vapour pressure data above 1 atm. as reported in the original treatise (Mellor, VIII, 59) are probably in error because of the temperature scale prevailing at the time. Michels points out that Friedman and White's critical data do not agree with the rest of their vapour pressure data and also that the equation they propose is not a very good representation of their own results.

Below 1 atm. the results of Armstrong agree very well with those of Keesom and Bijl and of Giauque and Clayton, the deviations being systematic and attributed by Armstrong to the different temperature scales used in the several laboratories.

The National Bureau of Standards[80] has also reported values based on the data of the authors in Table IX and also earlier data reported previously (Mellor, VIII, 59).

Various equations have been proposed by some of the above workers, which relate vapour pressure and temperature.

Michels *et al.* deduced the equation:

$$\log_{10}P = A/T = B\log_{10}T + CT + D$$

where $A = -634{\cdot}337$, $B = -15{\cdot}33647$, $C = 0{\cdot}0332183$ and $D = 34{\cdot}58230$.

Armstrong found that his results for the temperature range boiling-point to triple point fitted an Antoine-type equation.

$$\log P_{mm} = 6{\cdot}49594 - \frac{255{\cdot}821}{T-6{\cdot}600}$$

Kirshenbaum's study also includes vapour pressure data for liquid containing 34·6% ^{15}N as well as for natural nitrogen. The relation in the vapour pressure of natural nitrogen (P_1) and samples containing 34·6% ^{15}N (P_2) is given by:

$$\log (P_1/P_2) = (0{\cdot}2474/T) - 0{\cdot}00199,$$ [135–139]

whilst the ratio of the vapour pressures of pure ^{14}N and ^{15}N isotopes is given by

$$\log (P_{14}/P_{15}) = (0{\cdot}7230/T) - 0{\cdot}005822$$

Other values for the boiling point, triple point and transition point (i.e. α-solid → β-solid) which have not been included in Tables IX and X are given in Table XI below.

Table XI.—Boiling Point, Triple Point and Transition Point of Nitrogen

Year	Authors	Pressure, mm.	Transition Temp., °C.	Triple Point, °C.	Boiling Point, °C.	Ref.
1929	Clusius		−237·8	−210·12		2
1931	Justi	93·91		−210·07		140
1932	Heuse & Otto				−195·814	141
1933	Giauque & Clayton		−237·55			1
1935	Aoyama & Kanda				−195·833	142, 143
1936	Henning & Otto	94·6		−210·02	−195·808	144, 145
1955	Furukawa & Park			−209·98		126

The National Bureau of Standards[80] gives a normal boiling point of 77·395°K., but it is thought that a value of 77·35°K. based on Armstrong's work is more reliable.[79]

From Tables IX, X and XI reasonable values for the triple point constants would be[79] $P_{TP} = 94{\cdot}01$ mm.; $T_{TP} = 63{\cdot}15$°K.; the National Bureau of Standards gives values of 94·0 mm. and 63·156°K., respectively, which are in good agreement.

Kirshenbaum and Urey[139] report triple-point pressures of 9·386 cm., and 9·378 cm. respectively for natural nitrogen and nitrogen containing 34·6% ^{15}N. It is inferred that the triple point of pure ^{15}N is 0·058°C. higher than that of pure ^{14}N and that the boiling point is 0·052°C. higher.

Friedman *et al.*[136, 137] report the following values for the critical constants: $P_c = 33{\cdot}54 \pm 0{\cdot}02$ atm., and $T_c = 126{\cdot}00 \pm 0{\cdot}04$°K. The National Bureau of Standards values,[80] based on older determinations, are $P_c = 33{\cdot}49$ atm. and $T_c = 126{\cdot}1$°K. A more reasonable value would be 126·2°K.[79]

Van Dranen[146] has shown that the predicted value of the van der Waals part of the potential energy (U_c) at the critical point is −455 g.-cal./mole as compared with a value of −453·5 g.-cal./mole extrapolated from the experimental results of Michels. This lends support to the hypothesis that the critical state arises from the fact that at the critical point the average kinetic energy is equal to the average potential energy.

VARIATION OF MELTING POINT WITH PRESSURE

Table XII gives the pressure ranges and corresponding melting points observed by various workers.

Table XII.—Variation of Melting Point of Nitrogen with Pressure

Year	Author	Pressure	Melting Point, °K.	Ref.
1930	Simon, Ruhemann & Edwards	0 kg./cm^2 4870 kg./cm.^{2}	62·2 130	128, 129
1934	Keesom & Lisman	17·0 kg./cm.^{2} 111·1 kg./cm.^{2}	63·5 65·5	130, 131
1931	Verschoyle	0·12 atm. 205·42 atm.	63·2 67·64	147
1934	Bridgman	1 kg./cm.^{2} 6000 kg./cm.^{2}	63·14 149·2	71, 148
1937	Benedict	1930 atm. 5708 atm.	98 148	75
1954	Robinson	1 atm. 9000 atm. 10,000 atm.	63·1 179·5 190·0*	149

* Extrapolated value.

Robinson fitted his results by the equation

$$\frac{P}{a} = \left(\frac{T}{T_0}\right)^c - 1$$

where $a = 1800$ atm., $c = 1775$ and $T = 637$°K.

In a more recent paper Mills and Grilly[150] report further data on the effect of pressure (0 – 3600 kg./cm.^{2}) on the melting point of nitrogen, and show that they are expressed by the equation

$$P = a + bT^c$$

where $a = 1638{\cdot}30$, $b = 0{\cdot}976786$, $c = 1{\cdot}791000$.

There is good agreement between the results of Keesom and Lisman and of Verschoyle. Benedict and Bridgman, using the same apparatus, obtained good agreement, but their results differ from those reported by Simon, by Ruhemann and Edwards and by Robinson. Assuming pressure and temperature measurements to be correct, the method used by Robinson seems to be the least liable to error; his results are therefore recommended.[79]

Bridgman[71, 148] also quotes values of other melting point parameters, viz., specific volume of freezing liquid and solid and latent heats. Benedict[75] also gives specific volume data for the freezing liquid. He points out that his curve for volume against temperature does not show the very marked inflexion found by Bridgman at 1000 and 2000 kg./cm.^{2}; there appears to be some inaccuracy in Bridgman's results.

Bridgman states that the melting point parameters resemble those for other normal substances, and give no experimental indication of an approaching critical point between liquid and crystal, or of a maximum or asymptotic temperature; rather they indicate a melting curve rising to indefinitely high temperatures and pressures.

At the triple point Keesom and Lisman[130, 131] calculated a figure of 0·947 g./cm.^{3} for the density of the solid from the slope of their melting curve using the Clausius–Clapeyron equation and Giauque and Clayton's latent heat of fusion.

Various equations of state for liquid nitrogen have been proposed, and some physical properties of solid nitrogen and liquid nitrogen have been deduced from theoretical considerations.[35–39]

SPECIFIC HEAT OF GASEOUS NITROGEN

Experimental Data for C_p

Table XIII gives some of the results obtained by various workers for the specific heat of gaseous nitrogen either by experiment or by calculation. In some cases discussed below the original paper also gives values of the velocity of sound in nitrogen, where this method has been used in the determination of the specific heat. The figure 0 given as the pressure refers to the ideal gas state. For an appraisal of the methods available, the reader is referred to Partington's *Advanced Treatise of Physical Chemistry*, Vol. I.

Table XIII.—Specific Heat of Gaseous Nitrogen

Year	Observers	Method	Temperature °C.	Pressure, atm.	C_p g.-cal./mole	C_v g.-cal./mole	$\gamma = C_p/C_v$	Ref.
1928	Shilling & Partington	Velocity of sound	16 1000	1	6·92	4·92	1·405	156
1929	Chopin	Circulation calorimetry	0 to 200 0 to 1000	1	6·95 7·39			157 158
1929	Eucken & von Lüde	Adiabatic expansion	31·4 203·7	1	6·94 9·982			160 160
1929	Newitt	Explosion	16 to 2327 16 to 2727			5·87 6·01		161
1933	Okamura	Flow calorimetry	20 180	1	6·950	4·97 5·06		162
1931	Henry	Flow calorimetry	0 350	1		4·96 5·33		159
1932	Eucken & Mücke	Adiabatic expansion	208 418	4·06 4·06	7·034 7·327			163
1932	Keesom & van Lammeren	Velocity of sound	−190·2 −107·2	0 1·0090			1·400 1·400	83
1934	Johnston & Davis	Spectroscopic statistical	−223 1273	0	6·995 7·821			164
1932	Kelley	Spectroscopic statistical	−173 21	0	7·16 6·98			165
1934	Trautz & Ader	Spectroscopic statistical	−273 600	0		4·9673 5·6325		166
1937	Van Itterbeek & Mariëns	Velocity of sound	180·02	0		1·399		167 84
1937	Hubbard & Hodge	Velocity of sound	270	0 100			1·403 1·564	168, 169
1940	Clark & Katz	Resonance	230	0			1·4006	170, 171
1950	Koehler	Oscillation	25	1			1·4029	172

The values obtained from spectroscopic data by Johnston and Davis[164] and by Kelley[165] do not agree with each other nor with the results obtained experimentally by other workers. The agreement among the experimental results of the several authors is, however, fairly good.[79]

For the variation of C_p with temperature Chopin[157, 158] suggested the equation

$$C_p = 6{\cdot}82 + 0{\cdot}00058T$$

as compared with Kelley's equation[157]:

$$C_p = 6{\cdot}50 + 0{\cdot}001T$$

The variation of γ $(= C_p/C_v)$ with pressure at 23°C. is expressed by Clark and Katz[170, 171] in the equation

$$\gamma = 1{\cdot}4006 + 2{\cdot}21 \times 10^{-3} P$$

Refs. p. 48

Johnston and Davis[164] consider that the rotational heat capacity curves for nitrogen and carbon monoxide, as determined from spectroscopic data, show maxima at about 2° and 5°K., respectively. The existence of ortho and para rotational states in nitrogen produces heat capacity curves similar to those for the ortho–para equilibrium in non-equilibrium forms of nitrogen.

From a general equation relating the specific heat at constant volume and the critical temperature it has been shown that C_v at the critical temperature is 11·3 g.-cal./mole degree.[173]

Effect of Pressure

By a continuous flow method the variation of C_p with pressure at constant temperature has been measured.[174–177] Some of the results of Mackey and Krase[175–177] are given in Table XIV.

Table XIV.—Variation of C_p for Nitrogen with Pressure

t°C.	Pressure, Atmospheres								
	1	50	100	200	300	400	500	600	700
20	6·91	7·41	7·92	8·64	8·94	9·07	9·12	9·14	9·16
100	6·94	7·21	7·48	7·92	8·23	8·35	8·39	8·43	8·45
150	6·96	7·19	7·36	7·66	7·89	8·02	8·13	8·20	8·25

From measurement of the Joule–Thomson effect in nitrogen, Roebuck and Osterberg[178] (see page 43) were able to calculate the values of C_p at various temperatures and pressures. Good agreement was obtained with the results of Mackey and Krase as well as with the data of Edwards, Deming and Shupe[179, 180]; the last authors calculated C_p values from PV–T data.

Other work of less importance on the specific heat of gaseous nitrogen has been reported[181–207]; this includes data on the velocity of sound in nitrogen[192–198] and general reviews[199–207] of the data quoted above.

Some measurements have also been made of the specific heats of various binary nitrogen gas mixtures.[208–212]

The National Bureau of Standards[80] have computed specific heats by combining ideal values (see page 48) with differences between the values of the real and ideal gas. Some of the ideal specific heats are as follows:

°K.	10	100	300	600	1000	2000	5000
$\frac{C^\circ_p}{R}$	3·5019	3·5004	3·5030	3·6214	3·9326	4·3268	4·5528

To obtain C°_p g./cal. mole^{-1}°K^{-1} (or °C.$^{-1}$) multiply C°_p/R by 1·98719.

Some of the real specific heats expressed as C_p/R and derived by the procedure outlined in the previous paragraph are given below.

°K.	0·01 atm.	1 atm.	10 atm.	100 atm.
100	3·5012	3·613	—	4·000
300	3·5031	3·5083	3·5565	4·021
1000	3·9326	3·9329	3·9361	3·9647
3000	4·4545	4·4545	4·4547	4·4561

To obtain C_p g.-cal.g.$^{-1}$°K.$^{-1}$ (or °C.$^{-1}$) multiply C_p/R by 0·0709305.

The National Bureau of Standards states that the accuracy of the tabulated values varies with temperature and pressure. The error in $(C_p - C^\circ_p)/R$ may approach 5% in the range of moderate pressure and 10% for the high pressure data and may be still greater at the lower temperatures. They further consider that the results of Shilling and Partington[156] derived from measurements of the velocity of sound at high temperatures are unreliable because of the effect of dispersion related to vibrational excitation.

Comparison of C_p and C_v

Values of C_p and C_v obtained by a smoothing technique have been reported by Michels.[81, 82] A selection of these data is given in Table XV, where C_p and C_v are given in g.-cal. mole^{-1} degree^{-1}.

Table XV.—Specific Heat (C_p and C_v) of Nitrogen

P, atm.	−125°C.		−50°C.		0°C.		50°C.		100°C.		150°C.	
	C_p	C_v	C_p	C_v	C_p	C_v	C_p	C_v	C_p	C_v	C_p	C_v
0	6·954	4·967	6·955	4·968	6·956	4·970	6·962	4·976	6·976	4·989	7·002	5·016
10	7·72	5·055	7·213	5·01	7·107	4·995	7·056	4·985	7·038	4·995	7·048	5·02
50	16·52	5·45	8·28	5·17	7·69	5·095	7·42	5·05	7·28	5·038	7·21	5·04
100	17·66	5·135	9·60	5·34	8·37	5·20	7·83	5·115	7·56	5·075	7·41	5·055
200	12·30	5·095	10·93	5·53	9·27	5·35	8·43	5·20	7·98	5·12	7·73	5·07
400	10·45	5·27	10·60	5·74	9·68	5·56	8·88	5·35	8·36	5·195	8·04	5·115
600	9·92	5·465	10·18	5·91	9·59	5·735	8·96	5·48	8·47	5·28	8·15	5·16
1000	9·51	5·71	9·82	6·20	9·43	6·00	8·92	5·695	8·50	5·43	8·19	5·25
2000	9·23	6·03	9·91	6·71	9·44	6·44	8·91	6·055	8·46	5·68	8·15	5·40
4000	—	—	—	—	9·75	6·96	9·09	6·425	8·58	5·95	8·20	5·605
6000	—	—	—	—	10·24	7·30	9·38	6·63	8·79	6·11	8·39	5·73

Values of γ for molecular nitrogen are reported by the National Bureau of Standards.[80] These values of γ are thought to be reliable to within 5% of their difference from the values for the ideal gas at pressures below 40 atm. and possibly only to within 10% of this difference at the highest pressure of 100 atm.; at the lowest temperatures the error may exceed 10% of the difference from the ideal values. A selection of these values of γ is given in Table XVI.

Table XVI.—Specific Heat Ratio of Nitrogen, $\gamma = C_p/C_v$

°K.	0·01 atm.	0·1 atm.	1 atm.	10 atm.	100 atm.
100	1·400	1·402	1·424	—	—
200	1·400	1·400	1·404	1·447	2·11
300	1·400	1·400	1·401	1·417	1·566
400	1·397	1·397	1·398	1·406	1·488
600	1·381	1·382	1·382	1·385	1·410
800	1·3601	1·360	1·360	1·360	1·372
1000	1·341	1·341	1·341	1·342	1·347
2000	1·301	1·311	1·301	1·301	1·301
3000	1·289	1·287	1·289	1·289	1·289

Measurements of the velocity of sound are also tabulated by the National Bureau of Standards and a selection of their data is given in Table XVII, expressed as a/a_0, where a_0 represents standard conditions, i.e. 0°C. and 1 atm.

At 200°K. the values are believed to be reliable to within about 0·002 at 10 atm., 0·01 at 40 atm., 0·03 at 70 atm. and 0·07 at 100 atm. At 400°K. these limits could be reduced by a factor of between 5 and 10. At higher temperatures the values for 100 atm. are probably reliable to within 0·005.

Table XVII.—Velocity of Sound (a/a_0) in Gaseous Nitrogen

°K.	0·01 atm.	0·1 atm.	1 atm.	10 atm.	100 atm.
100	0·605	0·604	0·598	—	—
200	0·855	0·855	0·855	0·851	0·94
300	1·048	1·048	1·048	1·052	1·129
600	1·472	1·472	1·473	1·480	1·558
1000	1·872	1·872	1·873	1·880	1·945
2000	2·608	2·608	2·608	2·613	2·660
3000	3·179	3·179	3·180	3·183	3·222

To convert a/a_0 to a (m.sec.$^{-1}$) multiply by 336·96.

A selection of the values of the velocity of sound in gaseous nitrogen as reported by Michels[81, 82] and expressed in m.sec.$^{-1}$ is given in Table XVIII.

Table XVIII.—Velocity of Sound in Gaseous Nitrogen

Pressure, atm.	−125°C.	−50°C.	0°C.	50°C.	100°C.	150°C.
0	248·1	304·6	337·0	366·3	393·4	418·7
10	240	304	338	368	396	421
100	362	326	362	394	422	449
400	776	580	549	547	557	571
1000	1092	917	863	833	820	817
2000	1408	1250	1197	1161	1140	1130
6000	—	—	—	1984	1978	1970

SPECIFIC HEAT OF THE CONDENSED PHASES

The specific heat at constant pressure, C_p, cannot be directly measured since, if the pressure remained constant (i.e. saturated vapour pressure), the solid or liquid would melt or evaporate; the values obtained under these conditions would be largely latent heats and not specific heats. It is useful therefore to determine a more practical specific heat, C_σ, which is the specific heat at constant saturation, i.e. of the solid and liquid in equilibrium with an infinitesimally small volume of vapour. In this case the pressure and temperature rise according to the vapour pressure relationship. At low temperatures where the vapour pressure is low, C_σ and C_p are almost identical.

Specific Heats of Liquid and Solid Nitrogen

Table XIX gives some of the values of C_σ obtained by various workers. All three sets of data are in good agreement.

Some measurements of the velocity of sound in liquid nitrogen have been reported.[214–218]

Latent Heats

Table XX gives the latent heats of transition, fusion and vaporization of nitrogen reported by various workers.

Kirshenbaum[135, 139] has reported that the heat of vaporization of $^{15}N_2$ is 3·33 g.-cal. higher than that of $^{14}N_2$ whilst the heat of vaporization of nitrogen containing 34·6% of ^{15}N is only 1·14 g.-cal. higher than that of natural nitrogen.

Ducloux[220] has developed a theory for calculating the heat of liquefaction of a gas, from compressibility measurements above the critical temperature. The almost

Table XIX.—Specific Heats of Solid and Liquid Nitrogen

Year	Authors	Temperatures, °K.	$C_p = C_\sigma$	Ref.
1929	Clusius	10·42 (α-solid) 34·3 (α-solid) 38·8 (β-solid) 61·0 (β-solid) 66·9 liquid 73·5 liquid	1·362 10·20 8·951 11·09 13·54 13·69	2
1930	Wiebe & Brevoort	79·17 liquid 116·99 liquid	13·76 18·72	213
1933	Giauque & Clayton	15·82 (α-solid) 35·33 (α-solid) 39·13 (β-solid) 61·40 (β-solid) 65·02 (liquid) 77·74 (liquid)	3·124 10·67 8·948 11·09 13·33 13·64	1

Table XX.—Latent Heats of Transition, Fusion and Vaporization of Nitrogen

Year	Authors	Pressure, atm.	Temperature, °K	ΔH Transition, k.cal./mole	ΔH Fusion, k.cal./mole	ΔH Vaporization, k.cal./mole	Ref.
1929	Clusius	1	63·08 35·4	 0·0514	0·171		2
1933	Giauque & Clayton	1	63·14 77·32 35·61	 0·0547	0·172	 1·698	1
1935	Aoyama & Kanda	1	63·1 63·1		0·171	1·442	132, 133
1950	Friedman & White	1	77·34			1·320	136, 137
1953	Furakawa & McCoskey					1·337	219

quantitative agreement for nitrogen between the theoretical and experimental figures is attributed to a fortunate compensation of errors.

JOULE–THOMSON COEFFICIENT

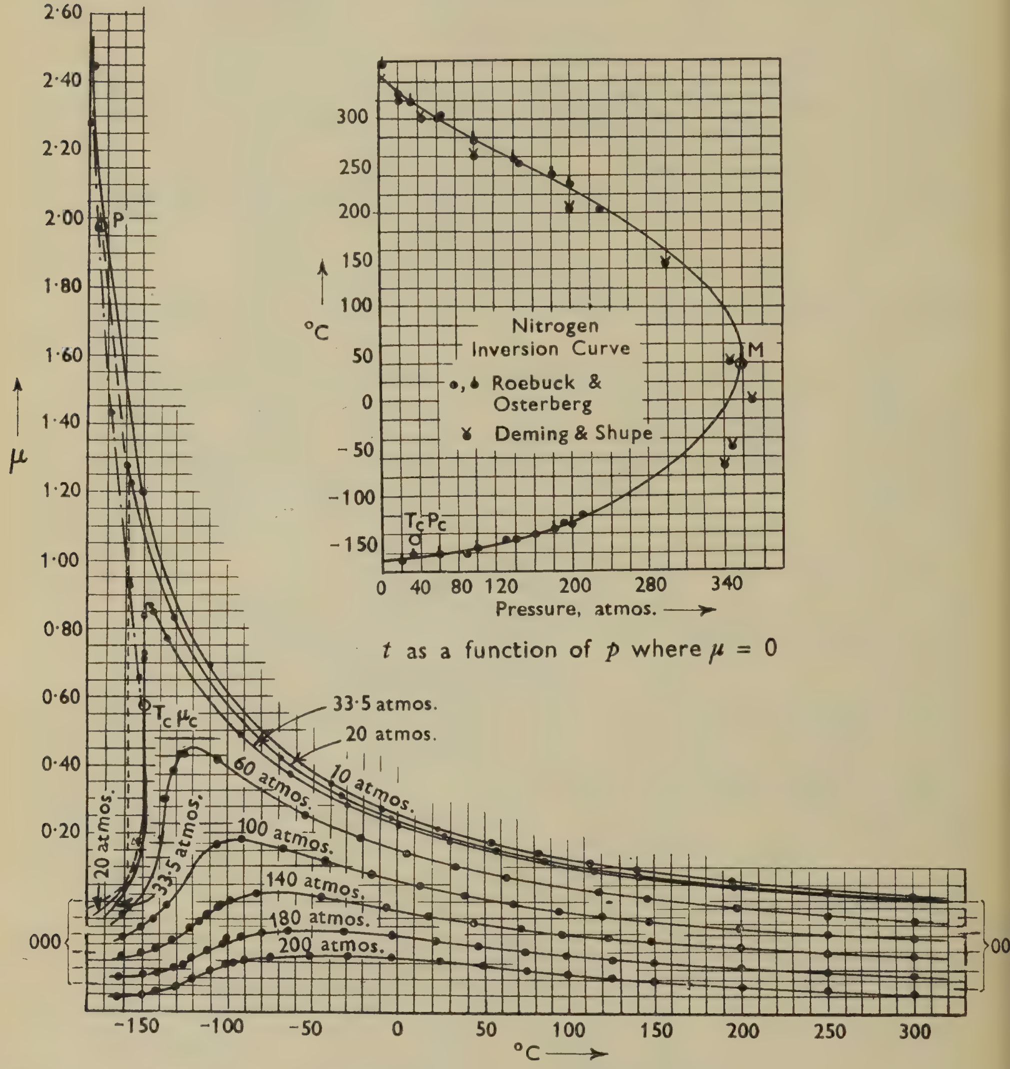
The Joule–Thomson coefficient

$$\mu\left[\equiv\left(\frac{\partial T}{\partial p}\right)_H\right]$$

from −150° to 300° and 1 to 200 atm. have been determined experimentally by Roebuck and Osterberg[178]; their results are given with the inversion curve in Fig. 2. [In this paper all the tabulated pressure values need correction (by multiplying by 0·9677) for an incorrectly calibrated pressure gauge; all functions of pressure also need correction.]

The inversion curve also shows the results of Deming and Shupe,[179] obtained by calculation, with which there is reasonable agreement. A later paper by these authors[180] gives corrected values of μ, and agreement with Roebuck. Osterberg's practical data are good.

Michels *et al.*[81, 82] calculated values for the adiabatic Joule–Thomson coefficient (μ) from their smoothed P–V–T data; a selection of their data is given on page 45.



t as a function of *p* where $\mu = 0$

μ as a function of *t* at constant pressure

FIG. 2.—Joule–Thomson effect in Nitrogen

The isothermal Joule–Thomson coefficient $(\partial H)/(\partial p)_T$ has been measured by expansion through a fine electrically heated metal capillary. The results of Collins and Keyes[221] are only from 2 to 1 atm. at 30°, 40° and 75°C. Gusak[222] reports results for pressures between 60 and 200 atm. at temperatures between 115 and 291°K. Charnley, Isles and Townley[223] have described a new apparatus for measuring

Pressure, atm.	Joule–Thomson coefficient μ of nitrogen in degrees, atm.$^{-1}$				
	−125°C.	−50°C.	0°C.	50°C.	150°C.
0	0·775	0·406	0·271	0·184	0·087
100	0·203	0·235	0·172	0·117	0·0526
1000	−0·0590	−0·0532	−0·0545	−0·0559	−0·0607
6000	—	—	−0·0553	−0·0604	−0·0677

the isothermal Joule–Thomson coefficient. The temperature range 0° to 45°C. and the pressure range 0 to 45 atm. were covered, and these authors claim that the results agree well with other direct measurements and with adiabatic Joule–Thomson and compressibility data.

The isothermal Joule–Thomson effect for nitrogen–helium[224] and nitrogen–methane[225] mixtures has been reported.

ENTHALPY, ENTROPY AND FREE ENERGY

Thermodynamic diagrams and tables of thermodynamic functions have been evaluated by various authors from selections of the preceding data which they personally considered to be the best available at the time of preparation.[81, 82, 222, 226–254]

The data of Din[235] are the most comprehensive available and embrace all the available practical data from the normal boiling point to 700°K. and from 1 atm. to 10,000 atm.

The most recent measurements are those of Woolley (National Bureau of Standards),[80] who has presented tables obtained from a correlation of some of the existing experimental data via the virial coefficient equation

$$Z = PV/RT = 1 + B_1P + C_1P^2 + D_1P^3$$

The virial coefficients B_1 and C_1 were obtained through the use of the Lennard-Jones 6:12 potential. The coefficient D_1 was represented by an equation fitted to the data of state. It was not possible to obtain an exact fit of the second virial coefficient to all the best data using an unmodified Lennard-Jones function. Nevertheless such a function was used since the tables were intended primarily for moderate and elevated temperatures; at lower temperatures, the correlated results departed considerably from the data. The parameters used to obtain C_1 and the function D_1 were so chosen as to compensate partially for the failure to fit B_1 to the actual P–V–T data at moderately low temperatures. The reliability of these tables is stated to be as follows: in the region from about 0° to 150°C., where the most accurate experimental determinations have been made, the uncertainties of the tabulated values are smallest; the uncertainty does not exceed 0·1% in PV/RT and may be as low as 3% of the difference between the real and ideal values of the compressibility factor in this region, increasing considerably both at higher and at lower temperatures.

The compressibility tables are in essential agreement with the correlations of Hall and Ibele[90] and Michels *et al.*[81, 82] The accuracy of the Bureau of Standards' tabulated values of enthalpy and entropy varies with temperature and pressure, and the uncertainty in the difference between real and ideal properties is thought to be somewhat less than 5% in the range of moderate pressure and may be as great as 10% at the highest pressure.

The thermodynamic properties of molecular nitrogen (expressed as the ideal gas) have been tabulated by the Bureau of Standards: these were obtained from spectroscopic measurements and by the use of statistical mechanical formulæ.

Tables XXI and XXII give selections from the tables for enthalpy (expressed as $(H-E_0°)/RT_0$ and entropy (expressed as S/R) respectively.

Table XXI.—Enthalpy $(H-E_0^\circ)/RT_0$ of Nitrogen

°K.	0·01 atm.	0·1 atm.	1 atm.	10 atm.	100 atm.
100	1·2777	1·2761	1·2589	—	—
200	2·5593	2·5588	2·5535	2·4999	1·94
300	3·8412	3·8409	3·8385	3·8140	3·596
400	5·1257	5·1256	5·1244	5·1125	5·013
600	7·7335	7·7335	7·7334	7·7331	7·7393
800	10·4423	10·4423	10·4428	10·4477	10·5020
1000	13·2674	13·2674	13·2683	13·2760	13·3573
2000	28·5356	28·5356	28·5370	28·5498	28·6779
3000	44·6437	44·6437	44·6452	44·6591	44·7976

The enthalpy function is divided here by a constant RT_0 where $T_0 = 273{\cdot}16$°K.; E_0° = internal energy of the ideal gas at absolute zero. To calculate $H-E_0^\circ$(g.-cal.g.$^{-1}$) multiply $(H-E_0^\circ)/RT_0$ by 19·3754.

Table XXII.—Entropy (S/R) of Nitrogen

°K.	0·01 atm.	0·1 atm.	1·0 atm.	10 atm.	100 atm.
100	23·8092	21·5037	19·1705	—	—
200	26·359	23·9328	21·6249	19·2682	16·382
300	27·6557	25·3529	23·0482	20·7248	18·230
400	28·6650	26·3623	24·0586	21·7454	19·3448
600	30·1077	27·8051	25·5020	23·1953	20·8548
800	31·1710	28·8084	26·5656	24·2609	21·9396
1000	32·0313	29·7287	27·4260	25·1223	22·8094
2000	34·9065	32·6039	30·3013	27·9986	25·6953
3000	36·6888	34·3862	32·0836	29·7810	27·4790

To calculate S, g.-cal.g.$^{-1}$°K.$^{-1}$ (or °C.$^{-1}$), multiply S/R by 0·0709305.

The recent table (1952) of Michels,[81, 82] which is based mainly on Michels' own P–V–T data, and also the data of Benedict[75] cover a much larger pressure range (up to 6000 atm.) than the tables of the National Bureau of Standards. Michels states that his tables are in good agreement with the data of Keesom *et al.*,[226] and, as stated above, the Bureau reports that their values are in essential agreement with Michels in the same pressure range.

A selection of Michels' entropy data is given in Table XXIII.

Table XXIII.—Entropy of Nitrogen—Michels' Data

P, atm.	−125°C.	−50°C.	0°C.	50°C.	100°C.	150°C.
1	−4·279	−1·410	0·000	1·172	2·176	3·054
10	−9·111	−6·075	−4·628	−3·438	−2·424	−1·538
100	−17·038	−11·493	−9·692	−8·332	−7·225	−6·284
200	−18·484	−13·497	−11·463	−9·981	−8·801	−7·815
600	−20·375	−16·222	−14·209	−12·652	−11·396	−10·352
1000	−21·333	−17·336	−15·370	−13·830	−12·572	−11·526
2000	−22·837	−68·909	−16·942	−15·404	−14·152	−13·110
4000	—	—	−18·669	−17·078	−15·807	−14·753
6000	—	—	−19·790	−18·186	−16·881	−15·805

The entropy at 0°C. and 1 atm. is taken arbitrarily to be 0·000.

The calculation of the ideal gas thermodynamic properties of nitrogen, entirely from spectroscopic data, has been reported by several authors.[1, 80, 256–258] A selection of values given by the National Bureau of Standards[80] is given in Table XXIV.

Table XXIV.—Ideal Gas Thermodynamic Functions for Molecular Nitrogen

°K.	$\frac{(H^\circ - E^\circ)}{RT_0}$	S°/R	$\frac{-(G^\circ - E^\circ)}{RT}$
10	0·1246	11·1440	7·740
100	1·2779	19·2043	15·714
200	2·5594	21·6308	18·135
300	3·8412	23·0505	19·553
400	5·1257	24·0598	20·560
600	7·7335	25·5025	21·982
800	10·4423	26·5658	23·000
1000	13·2674	27·4261	23·802
2000	28·5356	30·3013	26·404
3000	44·6437	32·0836	28·019
4000	61·0759	33·3745	29·204
5000	77·6941	34·3873	30·143

The enthalpy function is here divided by a constant RT_0 where $T_0 = 273{\cdot}16$°K.

Free energy and entropy values calculated from spectroscopic data have been tabulated for the temperature range 5000°K. to 20,000°K. by Döring.[31] In the temperature range 1000°K. to 25,000°K. the thermodynamic properties of a gas are of interest in the study of high-intensity shock waves. Beckett and Haar[259] have calculated the ideal gas thermodynamic properties of the nitrogen molecule and the nitrogen molecule ion for this temperature range.

Giauque and Clayton[1] using their own heat capacity data have estimated the entropy of nitrogen as follows:

"0–10°K. Debye function, $(h\nu/k) = 68$	0·458 E.U.
10–35·61°K. graphical (solid)	6·034
Transition 54·71/35·61	1·534
35·61–63·14°K. graphical (solid)	5·589
Fusion 172·3/63·14	2·729
63·14–Boiling point graphical (liquid)	2·728
Vaporization 1332·9/77·32	17·239
Total entropy for gas at b.p. (77·32°K.)	36·31 ± 0·1 E.U.
Correction for gas assuming Berthelot gas	0·22
Entropy of ideal gas at boiling point	36·53 E.U."

The entropy value at the boiling point calculated from band spectra by these authors (36·416 E.U.) is in good agreement with the calorimetric value. Giauque and Clayton state that at 298·1°K. the entropy is 45·9 E.U. (ideal gas) obtained by adding the spectroscopic increase of 9·4 E.U. to the calorimetric value of 36·53 E.U. The effect of nuclear spin has been neglected in the calculation; hence the limiting high temperature nuclear spin entropy apparently persists in the solid state at temperatures below 20°K. It appears also that nitrogen is not rotating in the solid state in a manner similar to hydrogen.

THERMODYNAMIC PROPERTIES OF ATOMIC NITROGEN

The thermodynamic properties of atomic nitrogen have been calculated from spectroscopic data using the methods of statistical mechanics.[80]

A selection of values from the National Bureau of Standards tables for the heat capacity at constant pressure, enthalpy function, entropy and free-energy function is given in Table XXV.

Table XXV.—Values of Specific Heat at Constant Pressure, Enthalpy Function, Entropy and Free Energy Function for Monatomic Nitrogen (Ideal Gas)

Temp., °K.	$\frac{C_p}{R}$	$\frac{(H^\circ - E_0^\circ)}{RT_0}$	$\frac{S^\circ}{R}$	$\frac{-(G^\circ - E_0^\circ)}{RT}$
10	2·5000	0·0915	9·9377	7·4377
100	2·5000	0·9152	15·6941	13·1941
200	2·5000	1·8304	17·4270	14·9270
300	2·5000	2·7456	18·4407	15·9407
400	2·5000	3·6609	19·1599	16·6599
500	2·5000	4·5761	19·7177	17·2177
600	2·5000	5·4913	20·1735	17·6735
700	2·5000	6·4065	20·5589	18·0589
1000	2·5000	9·1521	21·4506	18·9506
2000	2·5005	18·3047	23·1836	20·6835
3000	2·5216	27·4820	24·1998	21·6975
4000	2·6240	36·8689	24·9367	22·4189
5000	2·8235	46·8156	25·5422	22·9846

The enthalpy function is divided here by a constant RT_0 where $T_0 = 273{\cdot}16$°K.; E_0° (the internal energy of the ideal gas at absolute zero) is taken as the reference point of the enthalpy and free energy function.

Kirshenbaum[260] discussed the differences in the thermodynamic properties of liquid $^{14}N_2$ and liquid $^{15}N_2$ on the basis of several models of the Debye type.

THERMODYNAMIC PROPERTIES OF NITROGEN MIXTURES

Thermodynamic properties for the following mixtures are also reported:

nitrogen–hydrogen[68, 69, 261–281]
nitrogen–ammonia[282–285]
nitrogen–hydrogen–ammonia[261, 281–284]
nitrogen–water[274, 285]
nitrogen–oxygen[279, 286–290]
nitrogen–methane[272, 273, 276, 291–294]
nitrogen–hydrogen–methane[272]
nitrogen–ethylene[275, 295, 296]
nitrogen–propane[297]
nitrogen–helium[275]
nitrogen–carbon dioxide[268, 275, 298]
nitrogen–hydrogen–carbon dioxide[268, 277]

The statistical thermodynamic properties of multicomponent systems which include nitrogen have been determined.[299]

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OPTICAL REFRACTION

Refractive Index

Table XXVI gives the values for the refraction of light of different wave-lengths by nitrogen at 0°C. and 1 atmosphere pressure.

Table XXVI.—Refractive Index of Nitrogen at 0°*C. and* 1 *Atmosphere*

Authors	Year	Wave-length, A.	Refractive Index	Reference
Bennett	1931	4811 5893 6362	1·0002991 1·0002969 1·0002967	1
Tausz & Görlacher	1931	4358 5461 5876 6564	1·00030226 1·00029914 1·00029842 1·00029729	2
Bennett	1934	λ_∞ extrapolated	1·0002932	3
Essen & Froome	1951	—	1·002941*	4–6

*20°C. and 1 atmosphere.

The effect of pressure on the refractive index of nitrogen for radiation of different wave-lengths is reported,[7, 8] and a selection of typical data is given in Table XXVII.

Table XXVII.—Effect of Pressure on the Refractive Index of Nitrogen at 25°C.

Pressure, Atmospheres	Refractive Index	
	λ=6678 A.	λ=4471 A.
1	1·0002720	1·0002759
61·164	1·01663	1·01694
162·332	1·04318	1·04378
405·76	1·08869	1·09028
528·50	1·10380	1·10562
750·74	1·12377	1·12586
894·59	1·13373	1·13592
1138·12	1·14696	1·14926
1646·03	1·16703	1·16954
2053·07	1·17884	1·18161

Plots of the Lorentz–Lorenz function,

$$L = (n^2-1)/(n^2+2)\rho$$

versus pressure are reported in the same papers.[7, 8] Bennett[9] reports that the Lorentz–Lorenz function is constant for densities up to 0·01656 g./c.c., and quotes a mean value of $L = 0{\cdot}15596 \pm 0{\cdot}00008$.

The Kerr Effect

Guillien[10, 12] has determined, for liquid nitrogen, values of Kerr's constant (B) for the mercury green line (λ = 5461 A.); a selection of his values follows:

T°K.	61·87	64·12	67·10	70·01	72·65	74·18	77·4
$B \times 10^9$	10·70	10·14	9·47	9·04	8·57	8·35	7·88

These values are less than those given by the Langevin theory.

The variation of the Kerr constant with pressure is reported.[13–15] Some of the more recent values of Kuss and Stuart[15] at 25·1°C. are as follows:

P, atm.	111·6	147·7	166·0	224·0	245·0	312·9	387·3	415·3
$B \times 10^{10}$	2·94	3·89	4·37	5·89	6·31	7·85	9·04	9·71

Values of the Kerr constant of oxygen/nitrogen mixtures for the mercury green line 5461 A., at temperatures of 65° to 78°K., are reported by Keesom and Guillien,[16] typical figures being as follows:

8·83% nitrogen	T°K.	78·70	64·70
	$B \times 10^9$	26·34	35·17
31·85% nitrogen	T°K.	78·60	64·70
	$B \times 10^9$	20·00	26·18
67·16% nitrogen	T°K.	78·05	64·55
	$B \times 10^9$	12·82	16·63
92·93% nitrogen	T°K.	77·37	64·02
	$B \times 10^9$	8·91	11·57

The experimental curves for B, as a function of composition, are a little below those deduced from the Langevin theory. This is attributed to the diminution of the birefringence of the oxygen per g.-mol.wt. below that at infinite dilution.

The Faraday Effect

The Verdet constant (λ) for pure liquid nitrogen has been determined over the temperature range 63·3° to 82·3°K. using the 5461 A. green line of mercury.

The values of λ range from $0{\cdot}490 \times 10^{-2}$ at 63·3°K. to $0{\cdot}443 \times 10^{-2}$ at 82·3°K.[17]; over this temperature range, and because of the temperature variation of density, the specific rotary power $[\lambda] = \lambda/d$ remained essentially constant at $0{\cdot}564 \times 10^{-2}$. The rotativity, $[\lambda]9n/(n^2+2)^2$, where n is the index of refraction, also remained nearly constant at about $0{\cdot}513 \times 10^{-2}$.

A selection of the results expressed as Verdet's constant obtained at different wave-lengths follows[18]:

Temperature = 0°C. Pressure = 157 cm. Hg.

Wave-length A.	3635	4000	5000	6000	7000	8000	9000	9875
Verdet constant λ	16·70	13·51	8·363	5·775	4·156	3·131	2·498	2·132

A study of the Faraday effect in nitrogen gas ionized by means of an electrode discharge[19] showed that, within the limits of experimental error, the rotations calculated from the electron concentration are in agreement with the measured values.

For mixtures of oxygen and nitrogen the birefringence increases more rapidly than the corresponding variation of the coefficient of magnetization; for very high dilutions it varies approximately with $1/(T^3)$.[20, 21]

ELECTRICAL AND MAGNETIC PROPERTIES

Magnetic Susceptibility

Table XXVIII gives values for the specific susceptibility of nitrogen.

Table XXVIII.—Specific Susceptibility of Nitrogen

Ref.	Author	Year	Temperature	Specific Susceptibility × 10^6
22	Vaidyanathan	1928	273°K.	−0·46
23	Bitter	1930	298°K.	−0·58
			88°K.	−0·53
24	Havens	1933	Room Temp.	−0·426

Bonet and Bushkovitch[25, 26] calculated the diamagnetic and paramagnetic terms in the susceptibility of nitrogen by the statistical method of Thomas and Fermi, corrected for exchange and correlation effect. The molar magnetic susceptibility of nitrogen is calculated to be $-24{\cdot}6 \times 10^{-6}$.

Bitter[23] states that if there is a permanent moment in nitrogen it is less than 1/25 of a Bohr magneton. The volume susceptibility of nitrogen is proportional to the pressure[27]; Bitter has further shown that the introduction of water as an impurity in very small quantities results in deviations from proportionality as observed by Glaser (Mellor, VIII, 67).

Shur[28] in a theoretical review discusses the classical and quantum theories of diamagnetism and the methods of calculation of the magnetic susceptibility. The experimental results for nitrogen are also compared.

Dielectric Constant

GASEOUS NITROGEN

The following values of the dielectric constant for gaseous nitrogen shown in Table XXIX have been obtained.

The work of Fox and Ryan[35] at ultra-high frequencies seems to show that there is no change in the dielectric constant with frequency.

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Table XXIX.—Dielectric Constant of Gaseous Nitrogen

Author	Year	N.T.P.	Remarks	Ref.
Forró	1928	1·000545	0°C. and 1 atm.	29
Andrews	1931	1·000589	0°C. and 1 atm.	30
Broxon	1931	1·000556	16·5°C. and 1 atm.	31
Michels & Michels	1932	1·000573	0°C. and 1 atm.	32
Michels, Jaspers & Sanders	1934	1·0005824	0°C. and 1 atm.	33
Watson, Rao & Ramaswamy	1934	1·000538	25°C. 0 to 1 atm.	34
Fox & Ryan	1940	1·00058	22°C. to 45°, 1 atm.	35
Hector & Woernley	1946	1·0005796	0°C. and 1 atm.	36
Froome	1951	1·0005883	20°C. and 1 atm.	4
Zieman	1952	1·0005870 ±0·0000020	0°C. and 1 atm.	37

Forró[29] investigated the constants of the Debye equation

$$(\epsilon-1)/(\epsilon+2)\ (T/d) = aT+b$$

and concluded that (*a*) the measure of the optical contribution to the dielectric constant is independent of temperature and that (*b*) the permanent dipole contribution is zero.

The variation of the dielectric constant of nitrogen with temperature and pressure is reported.[2, 9, 31, 33, 38] A selection of the results of Uhlig *et al.*[38] and Michels *et al.*[32, 33] is given in Table XXX.

Table XXX.—Variation of Dielectric Constant of Nitrogen with Temperature and Pressure

Temp.	Pressure, Atm.	ϵ
0°C.	20	1·01220
	60	1·03732
	100	1·06262
	250	1·11473
25·28°	1·02	1·00052
	41·06	1·02206
	254·74	1·12875
	590·34	1·22873
	702·08	1·25076
100°	1·43	1·00062
	40·81	1·01731
	221·50	1·08781
	590·25	1·18846
149·79°	1·04	1·00035
	40·97	1·01534
	254·87	1·08674
	702·00	1·18846
	1011·56	1·23391

Michels *et al.*[32, 33] concluded that at a given temperature the dielectric constant varies linearly with pressure and that the value of the Clausius–Mosotti expression

$$\left[\left(\frac{\epsilon-1}{\epsilon+2}\right)\frac{1}{d}\right]$$

is a constant with a mean value of 191×10^{-6}.

Broxon,[31] in agreement with the work of Michels, states that $(\epsilon-1)$ varies directly with pressure over the range of pressure (0 – 150 atm.) investigated.

LIQUID AND SOLID NITROGEN

The results of the determination by McLennan, Jacobsen and Wilhelm[39] of the dielectric constant of liquid nitrogen, at and above its freezing point, are given in Table XXXI.

Table XXXI.—Dielectric Constant of Liquid Nitrogen

°K.	ϵ
78·5	1·455
77·1	1·457
75·3	1·465
72·3	1·472
70·5	1·478
69·6	1·481
68·3	1·484
66·0	1·492
63·3	1·500

For solid nitrogen the same authors obtained a value of 1·515.

Guillien[40, 41] reports values of $\epsilon = 1{\cdot}4318$ at 78°K. and 1·4746 at 63·3°K. with a marked increase to 1·514 on freezing followed by a very slow increase as the temperature falls.

Further related work, such as the effect of a magnetic field on the dielectric constant and the application of measurements of the dielectric constant, has been reported.[42–49]

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Ionization Potential

Values of the ionization potential of the nitrogen atom and the positively charged nucleus are as follows[1]:

Transition	$N \rightarrow N^+$	$N^+ \rightarrow N^{2+}$	$N^{2+} \rightarrow N^{3+}$	$N^{3+} \rightarrow N^{4+}$
ev.	14·55	29·6	47·4	77·4
Transition	$N^{4+} \rightarrow N^{5+}$	$N^{5+} \rightarrow N^{6+}$	$N^{6+} \rightarrow N^{7+}$	
ev.	97·9	551·9	663	

Earlier values reported by Millikan and Bowen[2] are $N \rightarrow N^+$ 14·494 ev., $N^+ \rightarrow N^{2+}$ 29·56 ev., $N^{2+} \rightarrow N^{3+}$ 47·2 ev.

Electron Affinity and Electronegativity

Glockler[3] calculated from ionization potentials that the electron affinity of the free nitrogen atom ($N+e \rightarrow N^-$) is $+0{\cdot}04$ ev. Bartlett[4] using a similar procedure showed previously that the electron affinity of nitrogen would have a relatively low value. Bates[5] has recalculated electron affinities by Glockler's method using later values for the ionization potentials; his value for the electron affinity of nitrogen is $-0{\cdot}6$ ev., which he considers more reasonable because discharge tube experiments show that the existence of N^- is doubtful.

Related to ionization potential and electron affinity of the atom is its electronegativity. Mulliken defines this as the mean value of the energies of the reactions $N \rightarrow N^+ + e$ and $N^- \rightarrow N+e$; for the valence state $N(S^2p^2V_3)$ Mulliken gives an absolute value of $7{\cdot}40 \pm 0{\cdot}4$ and 0·28 ev. relative to hydrogen.[6] This would result in the following order of decreasing electronegativity: $F > O > N$, H. As derived by Pauling[7] from consideration of the 'extra ionic energy' of bonds between unlike atoms, the value for nitrogen is 3·0 as compared with values of 4·0 for fluorine, 3·5 for oxygen and 2·1 for hydrogen.

Ionization Potential and Ionic Mobility of the Nitrogen Molecule

The ionization potential of the molecule ($N_2 \rightarrow N_2{}^+ + e$) is 15·65 ev.[3, 4] This value obtained by Tate *et al.*[8,9] is in reasonable agreement with the later value of 15·50 ev. reported by Worley and Jenkins.[10]

Data on the mobility of the nitrogen molecule ion are reported.[11–19] Values of the mobility k_p of N_2^+ (defined as the speed of the ion in cm./sec. in a field of 1 volt/cm. for a gas pressure of 760 mm. Hg) at different temperatures are as follows[11]:

°K	587	500	407	292	169	90	77	65
k_p	6·45	5·35	4·11	2·67	1·25	0·501	0·412	0·327

Most experimental evidence indicates that the N_2^- ion cannot be formed. As seen above, the electron affinity of the nitrogen molecule is negative.

For pressures up to 90 kg./sq. cm., breakdown voltages of up to $1{\cdot}5 \times 10^6$ v./cm. are required; and the magnitude of the breakdown voltage increases roughly linearly with the pressure.[20] At a pressure of 30 mm. Hg the breakdown potential is 1·66 kv. The distance between the electrodes is not given.[21, 22] Liquid nitrogen has a breakdown potential of 930 kv./cm. with platinum electrodes and 1000 kv./cm. with steel electrodes.[23]

For the pressure range 1800 to 6300 kg./cm.^{2} the resistivity varies from $3{\cdot}3 \times 10^7$ to $5{\cdot}3 \times 10^5$ ohm cm.[24] At 140 atm., nitrogen shows a very small conductivity with a field strength of 3750 v./cm., whilst at 75 atm. the field strength is less than 1400 v./cm.[25–27]

Further information on discharge tube phenomena will be found in the references 28–100.

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DIAMETER OF THE NITROGEN MOLECULE AND INTERATOMIC DISTANCE

Values of the collision diameter (σ) of the nitrogen molecule at different temperatures as calculated from the viscosity equation, $\mu = 0{\cdot}1792\ (kmt)^{1/2}/\sigma^2$ (where μ is the viscosity, m is the mass of the molecule, k is Boltzmann's constant) are given in Table XXXII.[1]

Table XXXII.—Collision Diameter of the Nitrogen Molecule

°K.	200	250	273	298	300	400	500	600	700	800	900	1000	1500	2000	2500
σ A.	3·968	3·826	3·776	3·733	3·730	3·605	3·529	3·476	3·428	3·409	3·387	3·369	3·315	3·287	3·270

Other values given for the diameter of the molecule range from 0·9 A. to 6·70 A.[2–7] Kaye and Laby[8] quote the following values:

3·7 3·5 3·6 3·1

which were calculated, respectively, from measurements of viscosity, thermal conductivity, van der Waals' constant b, and limiting density.

Values of the interatomic distance in the nitrogen molecule range from 0·91 A. to 2·28 A.[2, 9–20] A value of 1·108 A. has been calculated more recently[15, 16] from quantum mechanical considerations of the nitrogen molecule, and compared with an experimental value of 1·095 A.

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THERMAL CONDUCTIVITY

Gaseous Nitrogen

Table XXXIII gives a list of the reported measurements of the thermal conductivity of gaseous nitrogen at various temperatures and pressures.

Table XXXIII.—Thermal Conductivity of Gaseous Nitrogen

Year	Authors	Temperature, °C.	Pressure, atm.	Ref.
1928	Gregory & Marshall	0	1	1
1930	Wilner & Borelius	24 to 500	1	2
1937	Varhaftik	40 to 62	1 to 90	3
1939	Isikawa & Hijikata	—	<1	4
1946	Johnston & Grilly	−113 to +107	1	5
1946	Varhaftik & Oleshchuk	0 to 600	1	6
1947	Borovik	−183 to −102·5	33·5 to 100·5	7
1950	Stolyarov, Ipat'ev & Teodorovich	16 to 300	1 to 500	8
1951	Uhlir	−188 to −100	1 to 100	9
1953	Rothman	30 to 800	1	10
1953	Davidson & Music	0	1	11
1953	Lenoir, Comings & Junk	47 to 66	1 to 200	12, 13
1953	Michels & Botzen	25 to 75	1 to 2500	14
1955	Keyes	0 to −181	<10·6	15
1955	Rothman & Bromley	<775	1	16
1956	Varhaftik & Smirnova	50 to 530	—	17
1957	Johannin	75 to 700	1 to 1600	18
1958	Burton & Ziebland	−188 to −73	1 to 135	19

In the low temperature region the data of Uhlir[9] and of Burton and Ziebland[19] are in very good agreement; the data of the latter authors are presented in Fig. 3.

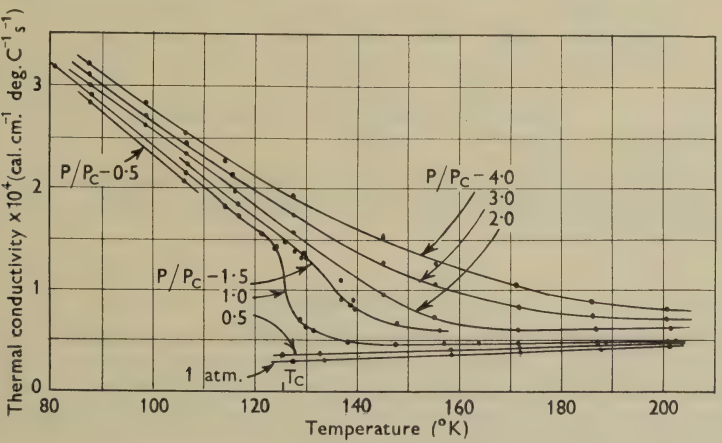

FIG. 3.—Thermal conductivity of nitrogen
$T_c = 126{\cdot}1_{35}$°K.; $P_c = 33{\cdot}49$ atm.

The results of Borovik,[7] however, appear to differ from those of the above authors and are thought to be slightly erroneous. At higher temperatures the results of Johannin[18] appear to be the most accurate, and his work is presented in Fig. 4.

The results of Stolyarov *et al.*[8] agree reasonably well with Johannin's data[18] but the data of Michels[14] do not. However, disagreement with Michels' work is also found in the results of Lenoir *et al.*[12, 13]

The National Bureau of Standards[20] have computed thermal conductivity values at atmospheric pressure from empirical formulæ fitted to the experimental data; a selection of their data is given below.

°K.	100	150	200	250	300	400	600	1200
k/k_0	0·390	0·576	0·753	0·924	1·081	1·377	1·890	2·968

(To obtain kg.-cal. cm.$^{-1}$ sec.$^{-1}$ °K.$^{-1}$ multiply k/k_0 by $5{\cdot}77 \times 10^{-5}$)

A review of some of the data on the thermal conductivity of nitrogen up to 1953 has been presented by Franck.[21, 22]

The thermal conductivity of the following gas mixtures has been reported: N_2–CO_2,[11, 29] N_2–H_2,[4] N_2–Ne,[11] N_2–He,[11] N_2–ethylene.[30]

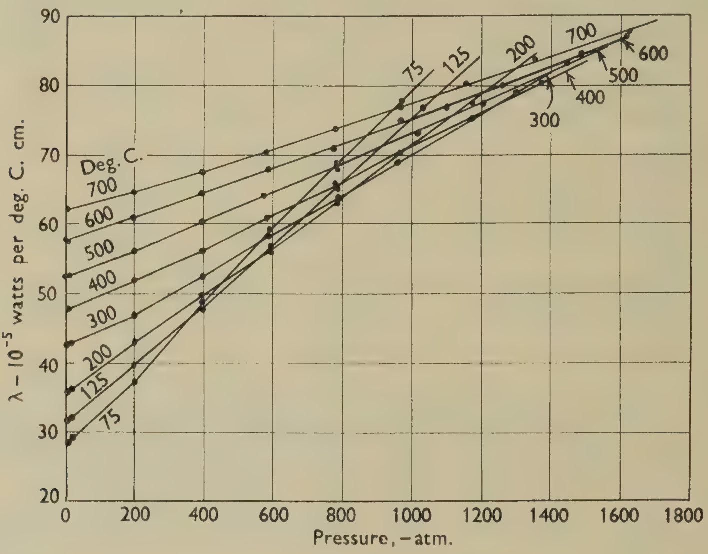

FIG. 4.—Thermal conductivity of nitrogen

The effect of an electrostatic field on the thermal conductivity of nitrogen is reported to be slight[31] as compared with the effect in gases consisting of molecules with large dipole moments.

Liquid Nitrogen

A few measurements have been made of the thermal conductivity of liquid nitrogen.[9; 19, 23–27] The data of Burton and Ziebland[19] and those of Uhlir[9] are in good agreement. The results of the former authors are given in Fig. 3. The data of Borovik[25] and Powers *et al.*[26] differ slightly from the above two sets of data, and the results of Hammann[24] are thought to be grossly in error.

Borovik[28] has formulated the following conductivity equation for liquid nitrogen:

$$\lambda = k_1[C_v + (9/4)R](W/r^2)$$

where λ = thermal conductivity,
R = 1·986 g.-cal/mole/degree,
W = velocity of sound,
r = radius of molecule,
k_1 = constant.

Refs. p. 67

Various data have been reported concerning the thermal accommodation coefficient.[32–45]

VISCOSITY

Gaseous Nitrogen

Determinations of the viscosity of gaseous nitrogen at atmospheric pressure made by several investigators are listed in Table XXXIV. Measurements made at higher pressures are listed in Table XXXV.

Table XXXIV.—Viscosity of Gaseous Nitrogen at 1 *Atmosphere*

Year	Authors	Temperature Range, °C.	Ref.
1929	Trautz & Baumann	−78 to 250	46
1930	Trautz & Melster	20 to 280	47
1930	Trautz & Zink	20 to 830	48
1931	Trautz & Heberling	100 to 250	49
1935	Van Itterbeek & Keesom	−183	50
1937	Fortier	−192 to 100	51
1938	Rigden	17	52
1938	Majumdar and Vajifdar	23	53
1940	Johnston & McCloskey	−180 to +20	54
1941	Wobser & Muller	+20 to −100	55
1943	Sibbitt, Hawkins & Solberg	20 to 400	56
1945	Vasilesco & Ribaud	0 to 1600	57–59
1951	Johnston, Mattox & Powers	−193 to +33	60
1954	Kestin & Pilarczyk	21	61

Table XXXV.—Viscosity of Gaseous Nitrogen at Different Pressures

Year	Authors	Temp. Range, °C.	Pressure, atm.	Ref.
1930	Boyd	500	190	62
1931	Michels & Gibson	25 to 75	10 to 966	63
1943	Sibbitt, Hawkins & Solberg	20 to 400	1 to 70	56
1951	Johnston, Mattox & Powers	−193 to +33	500 (mm.) to 0·0005 (mm.)	60
1951	Iwasaki	25 to 150	25 to 200	64,65
1954	Kestin & Pilarczyk	21	1 to 70	61
1957	Lazarre & Vodar	25 to 75	3000	66

Kestin and Pilarczyk[61] report a value at atmospheric pressure and at 21°C. of $\eta = 1755 \times 10^{-7}$ poise, which is in excellent agreement with the determinations of: Rigden,[52] 1756×10^{-7} poise; Johnston and McCloskey,[54] 1760×10^{-7} poise; and Vasilesco,[57–59] 1758×10^{-7} poise.

Below 300°K. the results of Fortier[51] and of Johnston and McCloskey[54] provide reasonably accurate coverage, Fortier's results probably being the more accurate. The work of Vasilesco *et al.*[57–59] appears to be highly accurate over the wide temperature range of 0° to 1600°C. The results obtained by the National Bureau of Standards (see below) confirm the foregoing appraisal of the experimental results.

For the pressure dependence of the viscosity of nitrogen the results of Sibbitt *et al.*[56] are some 3% lower than those of Kestin and Pilarczyk,[61] although there is excellent agreement as regards the slope of the curves of η versus pressure. In view of the excellent agreement among the various determinations of $\eta_{21°C.}$, the latter authors consider that Sibbitt's work contains a calibration error, as his value at 1 atm. is obviously too low.

Michels and Gibson's results[63] in the 10–15 atm. range are in excellent agreement with the data of Kestin and Pilarczyk,[61] but at higher pressures the values of the former authors are lower by about 2%. Because of the wide scatter in Boyd's results,[62] comparison is difficult, and in any case these results appear to fit badly with the data of other workers.

Kestin and Pilarczyk[61] have fitted the experimental results by the equation

$$\eta/\eta_a = 1+88{\cdot}79\times10^{-6}(P-14{\cdot}7)+9{\cdot}168\times10^{-10}(P-14{\cdot}7)^2 + 10{\cdot}86\times10^{-12}(P-14{\cdot}7)^3$$

where η is the viscosity at pressure P (pounds per sq. in.) and η_a is the viscosity at atmospheric pressure, all measured at 21°C.

Workers at the National Bureau of Standards[20, 67] have computed values at low pressures on the basis of the Lennard-Jones 6-12 intermolecular potential, for which Hirschfelder, Bird and Spotz have calculated the collision integral given by Chapman and Cowling. Above 600°K. the values thus computed were corrected for the systematic departure of the Lennard-Jones fit from the experimental data at high temperatures. For the pressure dependence of the viscosity of nitrogen the values were calculated on the basis of the Enskog theory. The values thus obtained (a selection of which is given in Table XXXVI) are in excellent agreement with the data of Kestin and Pilarczyk[61]; at room temperature and over the pressure range 1 to 70 atm. the agreement is said to be within 0·7%.

Table XXXVI.—Viscosity of Gaseous Nitrogen

°K.	η/η_0					
	1 atm.	10 atm.	20 atm.	40 atm.	60 atm.	100 atm.
100	0·413	—	—	—	—	—
150	0·607	—	—	—	—	—
200	0·779	—	—	—	—	—
300	1·074	1·079	1·086	1·104	1·127	1·187
400	1·323	1·329	1·334	1·347	1·362	1·399
600	1·752	1·757	1·762	1·769	1·778	1·800
800	2·099	2·102	2·105	2·112	2·119	2·135
1000	2·406	2·408	2·411	2·417	2·422	2·429
1500	3·040	3·042	3·044	3·048	3·052	3·061

To convert η/η_0 to η (poise) multiply by $1{\cdot}6625\times10^{-4}$.

Liquid Nitrogen

Few investigations[56, 68–73] have been made of the viscosity of liquid nitrogen. Most of the results have been obtained by Rudenko *et al.*,[71–73] and some of these are as follow:

T°K.	64	70	80	90	100	111·7
$\eta\times10^5$	210	226	149	116	94	74

Rudenko[73] reports that the fluidity of liquid nitrogen fulfils the empirical linear relation $\phi=a\theta+b$ where θ ($\equiv T/T_{\text{crit}}$) is the reduced temperature and a and b are constants.

Nitrogen Mixtures

The viscosities of the following mixtures have been determined:

(*a*) Gaseous nitrogen–hydrogen[46, 47, 62, 63, 74–77]
nitrogen–oxygen[47, 74]
nitrogen–carbon monoxide[47]
nitrogen–ethylene[47, 78]

nitrogen–carbon dioxide[78]
nitrogen–ammonia[79]
nitrogen–nitric oxide[74, 80]
nitrogen–helium[77]
nitrogen–freon[81]
nitrogen–hydrogen–freon[81]
nitrogen–carbon dioxide–freon[81]
nitrogen–hydrogen–carbon dioxide–freon[81]
(*b*) Liquid nitrogen–carbon monoxide[68, 69]
nitrogen–methane[68]
nitrogen–oxygen[70]

A considerable number of papers on the theoretical aspects of the viscosity of nitrogen have been published.[82–99] These are concerned mainly with the application of statistical mechanics and of the law of corresponding states.

The radius of the nitrogen molecule, according to Sutherland from viscosity-temperature data, is 3·28 A.,[99] whilst Michels and Gibson[63] reported a value of 2·94 A.

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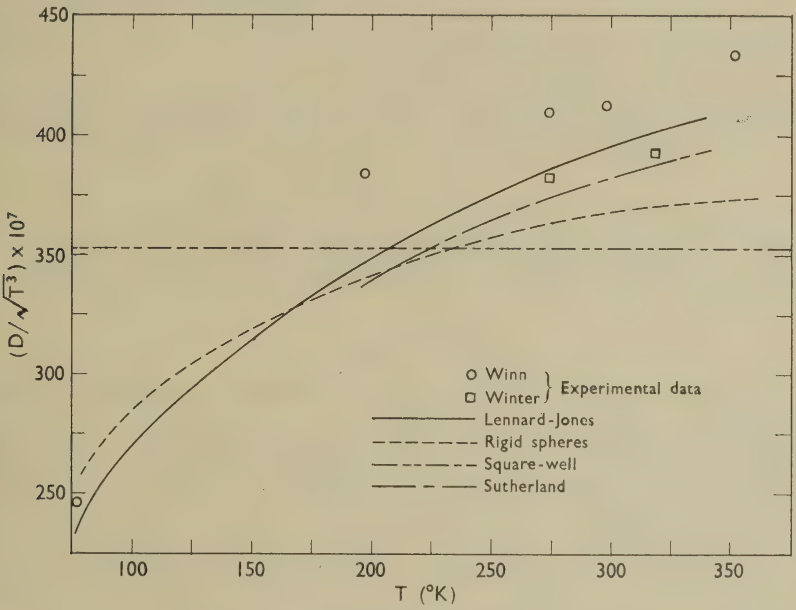

FIG. 5.—Coefficient of self-diffusion for nitrogen[3]

DIFFUSION OF NITROGEN

Self-diffusion

The coefficient of self-diffusion may be defined as a measure of the rate at which a group of gas molecules diffuses into another group of identical molecules.[1] Self-diffusion thus strictly defined cannot be observed experimentally, since if the molecules are identical there is no way of following the process. An experimental technique which can be used is the isotopic diffusion of ^{15}N into ordinary nitrogen; this process is believed to approximate closely to real self-diffusion. In addition, theoretical methods based on a molecular model (the most successful of which is the Lennard-Jones 12:6 model) have been established.

Using the isotopic technique, Winn[1] and Winter[2] report the values given in Table XXXVII for the self-diffusion coefficients; comparison is also made with theoretical calculations based on the Lennard-Jones 12:6 intermolecular potential. Fig. 5 gives the coefficient of self-diffusion for nitrogen as calculated for several molecular models and also the experimental data of Winn and Winter.

Table XXXVII.—Self-Diffusion Coefficient of Nitrogen

Temperature, °C.	Experiment, D, cm.^{2}/sec.	Calculated, D, cm.^{2}/sec.	Ref.
80·0	0·287	0·273	1
25·0	0·212	0·203	1
25·0	0·219	0·199	2, 3
20·0	0·185	0·174	1
0	0·172	0·172	2
−78·5	0·104	0·0946	1
−195·5	0·0168	0·0161	1

(D is referred to 760 mm. pressure)

An interesting result to compare with the above figures has been obtained by diffusion experiments on a nitrogen–carbon monoxide mixture.[4] Since nitrogen and carbon monoxide consist of molecules with nearly the same physical properties, the experiments are a close approximation to self-diffusion. A value of $D = 0{\cdot}211$ (15°C. and 760 mm. pressure) was obtained.

In a study of the self-diffusion of nitrogen at 20°C. and at pressures ranging from 20–90 atm., it was shown that the product of diffusion coefficient and gas density is independent of pressure.[5]

Diffusion of Nitrogen into Gases and Vapours

At 79°C. the diffusion coefficient for nitrogen into water vapour is 0·359[6, 57]; the plot of diffusion coefficient against temperature is linear up to 50°C. and is given by the equation

$$DP_0 = At + D_0$$

where D = diffusion coefficient at t°C., P_0 = total pressure in atmospheres, D_0 = diffusion coefficient at 0°C., and A = a constant.[6]

The diffusion coefficient of water vapour into nitrogen–hydrogen mixtures is reported.[6]

The values for the diffusion coefficient of nitrogen into various gases are given below in Table XXXVIII.

Table XXXVIII.—Diffusion of Nitrogen into Various Gases

System	Temp., °C.	Pressure, atm.	Diffusion Coefficient, cm.^{2}/sec.	Ref.	Calc. Value, cm.^{2}/sec.	Ref.
N_2–CO_2	0	1	0·144	7	0·130	3
	15		0·158	8	0·143	3
	20		0·16	9, 10	0·147	3
	25		0·165	11	0·152	3
N_2–CO	0	1	0·192	7, 12	0·174	3
N_2–O_2	0	1	0·181	7, 8	0·175	3
	20		0·22	9, 10, 13	0·199	3
N_2–A	20	1	0·20	9	0·188	3
	—	—	0·20	8, 10, 13		
N_2–H_2	0	1	0·674	7, 12,	0·686	3
	15	1	0·743	8	0·718	3
	20	1	0·76	10, 13	0·739	3
N_2–C_2H_6	25	1	0·148	11	0·144	3
N_2–C_2H_4	25	1	0·163	11	0·156	3
N_2–n-C_4H_{10}	25	1	0·0960	11	0·0986	3
N_2–*iso*C_4H_{10}	25	1	0·0908	11	0·0970	3
N_2 *cis*-butene–2	25	1	0·095	11	0·0947	3

From studies of the diffusion of nitrogen into mixtures of nitrogen and hydrogen and of carbon dioxide into mixtures of carbon dioxide and nitrogen at −21°, 0°, 17°, 25° and 35°C., the diffusion coefficient was found to increase with increasing concentration of the heavier component at all temperatures.[14, 15]

Resonance absorption of the sodium D line has been used to follow the diffusion of sodium vapour into nitrogen. At 253·5°C. and 1 atm. (nitrogen pressure = 4.3 mm.) the diffusion coefficient is 0·68 ± 0·03 cm.^{2}/sec.; this result is in good agreement with the earlier work of Hartel *et al.*[16] By using a method involving excitation and photographic measurement of the intensity of radiation of the metal vapour, the coefficient of diffusion for mercury vapour in nitrogen was found to be 0·14 cm.^{2}/sec. and that of cadmium vapour in nitrogen to be 0·17 cm.^{2}/sec. (both reduced to 8°C. and 760 mm. pressure).[17]

Other data involving the diffusion of nitrogen into bromine,[18, 19] iodine,[18] and oxygen[20] have been reported.

The interdiffusion through an orifice of nitrogen and hydrogen and of nitrogen and argon has been investigated.[21]

Diffusion of Nitrogen into Liquids

The rates of diffusion of nitrogen into degassed 1 to 3% solution of agar in water has been determined. The diffusion coefficient k is given by the equation

$$k = (v^2/4a^2)q^2t$$

where v is the volume of gas absorbed, a is the Bunsen absorption coefficient, q is the area of cross-section of the column of liquid and t is the time; it was observed that the value of k increases linearly with the temperature.[22]

Thermal Diffusion

NITROGEN ISOTOPES

The effect of temperature on the thermal diffusion of the nitrogen isotopes (in mixtures of $^{14}N_2$ and $^{14}N^{15}N$) is presented in Table XXXIX.[23] In addition the thermal diffusion factors predicted from the Lennard-Jones 13:7 force model are given. If the relative number density of the heavier molecules is n_{10} where the temperature is T, and n'_{10} where the temperature is T', and n_{20} and n'_{20} are corresponding quantities for the lighter molecules, then the ratio of n_{10}/n_{20} to n'_{10}/n'_{20} is the separation factor q[3, 24]

$$\alpha\ (\equiv \text{thermal diffusion factor}) = \frac{d(\ln q)}{d(\ln T'/T)}$$

$$R_T\ (\equiv \text{thermal separation ratio}) = \frac{\alpha}{[\alpha_\infty]}$$

where $[\alpha_\infty]$ is the value of α calculated for molecules which behave as rigid elastic spheres; (R_T) 13:7 is the calculated value of R_T based on the 13:7 intermolecular force model.

Table XXXIX.—Thermal Diffusion of Nitrogen Isotopes

Temperature, °K.	$\alpha \times 10^3$	(R_T), observed	(R_T) 13:7, calculated
434	9·1	0·58	0·54
329	7·1	0·47	0·44
286	5·1	0·33	0·48

NITROGEN–HYDROGEN MIXTURES

The work of Ibbs (Mellor, VIII, 56) has been continued by various investigators,[12, 25–39] and in addition the diffusion thermo-effect of hydrogen–nitrogen mixtures has been studied.[8, 13, 40–43] The diffusion thermo-effect is the phenomenon observed when gases which are at rest diffuse into one another; temporary temperature differences arise which disappear with progressive equalization of concentration (this is the so-called 'non-stationary' diffusion thermo-effect). In the case where the mathematical requirements of the so-called 'stationary' condition obtain, a permanent diffusion process takes place which results in the establishment of a constant temperature field (with respect to time); this is the so-called 'stationary' diffusion thermo-effect.[40] As an example of the magnitude of this effect, it is stated that at room temperature the temperature change for hydrogen–nitrogen mixtures is 7·5°C., which is much larger than the differential Joule–Thomson coefficient.[43]

Values of the thermal separation ratio (R_T) for the nitrogen–hydrogen system are given in Table XL.[12, 44]

Table XL.—Thermal Diffusion of Nitrogen Gas Mixtures

Gas	% of Lighter Constituent	T_r, °K.	$R_T \times 10^2$		Ref.
			Observed	Calculated	
N_2–He	34·5	145	7·42	7·12	12
	53·1	145	9·42	9·23	44
	34·5	261	8·31	7·65	
	53·1	261	10·7 (extrapolation)	9·92	
N_2–A	46	157	1·01	0·624	12, 44
	62·5	157	0·842	0·596	
	70	157	0·83	0·536	
	46	252	1·82	1·32	
	62·5	252	1·70	1·28	
	70	252	1·53	1·16	
N_2–H_2	29·4	143	3·95	3·97	12
	42·0	143	5·21	5·01	44
	77·5	143	4·84	4·44	
	29·4	264	5·48	5·90	
	42·0	264	7·49	7·37	
	77·5	264	6·63	6·36	
N_2–CO	50	324	1·53	0·05	12, 47

(Calculated values are based on 12:6 potential model of Lennard-Jones.) $T_r = \{TT'/(T'-T)\}\ln(T'/T)$; see also explanation of symbols for Table XXXIX.

The thermodiffusion factor at 1 atm. pressure and 20°C., for different ratios of hydrogen and nitrogen, ranges from 0·5 to 0·2.[8, 10, 13, 27]

The effect of pressure on the thermal diffusion factor of a nitrogen–hydrogen mixture is shown in Fig. 6.[26]

In an investigation[28] of the effect of a dissociating component on the thermal diffusion of a 50:50% nitrogen–hydrogen mixture, it was found that a separation of 13–14% could be obtained (hydrogen diffusing towards the hot end of the tube at 105°C., and nitrogen to the cold end at 30°C.), when 53% of nitrogen tetroxide and 47% of the nitrogen–hydrogen mixture were used; without the addition of the dissociating component the 50:50 nitrogen–hydrogen mixture gave only a 2% separation. When operating between 0° and 35°C. (at a total pressure of about 600 mm., using the same mixture of nitrogen tetroxide and nitrogen–hydrogen as above) a separation of barely 1% was obtained, the hydrogen diffusing towards the cold end and nitrogen towards the warm end.

In a theoretical discussion of the separation of hydrogen and nitrogen in the presence of nitrogen pentoxide,[25] the maximum relative separation was shown to occur at 320°K.

Hirota and Kobayashi[29] have reported separation of nitrogen–hydrogen mixtures by a continuous process based on thermal diffusion, and the values of the thermal diffusion factor thus obtained support the modified theory of Drickamer.

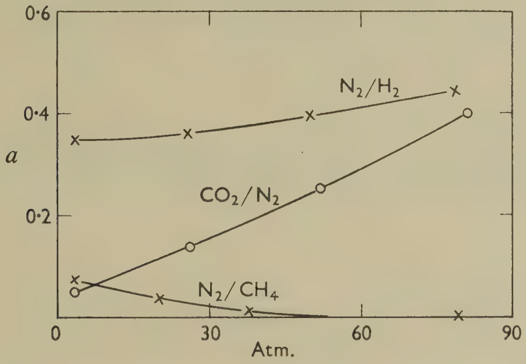

FIG. 6.—Effect of pressure on the thermal diffusion factor of binary nitrogen gas mixtures[26]

NITROGEN AND DEUTERIUM

Nitrogen–deuterium mixtures have been studied[35, 37, 41, 45] and in the temperature range 287–373°K.

$$\alpha = 0{\cdot}313 \quad \text{and} \quad R_T = 0{\cdot}58.^{45}$$

NITROGEN AND OXYGEN

For the nitrogen–oxygen system the values of α as determined from thermal diffusion data are +0·018 and −0·001 at 20° and −184°C., respectively. At 1 atm. and 20°C. the diffusion coefficient is 0·22.[8, 10, 13, 27, 38, 41, 42, 45, 46]

NITROGEN AND ARGON

Data on thermal diffusion and diffusion thermal effect have been reported for nitrogen–argon mixtures.[8, 10, 12, 13, 24, 27, 38, 41, 45, 46, 47, 48, 49] Some of the data are given in Tables XL (above) and XLI.

Table XLI.—Thermal Diffusion of Nitrogen Gas Mixtures

Mixture	(α_∞)	$\log_{10}(T'/T)$ T' (°K.)	−0·600 73·6	−0·500 92·7	−0·400 116·7	−0·300 146·9	−0·200 185·0	−0·100 232·8	0·000 293·0	0·200 465	0·400 736	0·600 1167
A–N_2 51·1% A	0·141	$\log_{10} q$ R_T	−0·012 −0·31	−0·016 −0·16	−0·017 −0·002	−0·016 −0·17	−0·013 0·31	−0·007 0·43	0·000 0·57	0·019 0·73	0·040 0·73	0·060 0·73
Kr–N_2 30·8% Kr	0·337	$\log_{10} q$ R_T	— —	— —	−0·019 0·02	−0·018 0·07	−0·014 0·14	−0·008 0·22	0·000 0·26	0·019 0·32	0·047 0·42	— —
N_2–CO_2 49·7%CO_2	0·236	$\log_{10} q$ R_T	— —	— —	— —	−0·003* −0·10	−0·004 −0·03	−0·003 0·08	0·000 0·19	0·013 0·33	0·031 0·039	0·049 0·39

* $\log_{10} T'/T = -0{\cdot}25$.

Values of α determined from the diffusion thermo-effect[46] are +0·071 and −0·022 at +20°C. and −184°C., respectively. At 1 atm. and 20°C. the diffusion coefficient is 0·20. As these results show, there is a reversal of sign in the thermal diffusion factor; the nitrogen–carbon dioxide system behaves similarly. A change of sign implies a change in the direction of diffusion—the heavier molecules diffusing up the temperature gradient instead of down the gradient, as is usual. A theoretical treatment based on the Lennard-Jones 13:7 force model accounts for this reversal of sign in the diffusion factor.[50]

NITROGEN AND KRYPTON

The separation factor (q) and thermal diffusion factor (α) for a 30·8% krypton–nitrogen mixture for different temperature gradients are given in Table XLI.[24] No reversal of sign was found for this system.

NITROGEN AND HELIUM

The thermal separation ratio of various nitrogen–helium mixtures is reported,[12, 44, 51] and some of the data are given in Table XL. In the temperature range 287° to 273°C. the thermal diffusion factor $(\alpha) = 0{\cdot}36$ and the thermal separation ratio $(R_T) = 0{\cdot}62$.[45]

NITROGEN AND CARBON MONOXIDE

Table XL gives the observed and calculated values of the thermal separation ratio R_T for a 50:50 mixture of nitrogen and carbon monoxide. Winter[12] states that the experimental values may well be inaccurate, since these two gases are very similar and their self-diffusion coefficients are both about 0·175 cm.^{2}/sec. at N.T.P. Further studies of the separation by thermal diffusion and the diffusion thermo-effect of nitrogen–carbon monoxide mixtures are reported.[38, 52]

NITROGEN AND CARBON DIOXIDE

Values of the thermal separation ratio (R_T) and the separation factor (q) for a nitrogen–carbon dioxide mixture (49·7% carbon dioxide) are given in Table XLI[24]; as with nitrogen–argon mixtures this system shows a reversal in sign in the values of R_T, implying a change in the direction of diffusion under certain conditions. At 1 atm. and 20°C. the thermal diffusion factor (α) is 0·039 and the diffusion coefficient is 0·16.[8, 10, 13, 27, 38, 41]

The effect of pressure on the thermal diffusion factor (α) is presented in Fig. 6.[26] Theoretical calculations for the pressure dependence of the thermal diffusion factor of the nitrogen–carbon dioxide system by Haase[26, 53, 54] are in agreement with Becker's experimental results; this indicates that an essential part of the pressure effect can be attributed to non-ideality of the gas mixtures.

NITROGEN AND METHANE, NITROGEN AND ETHYLENE

The effect of pressure on the thermal diffusion factor of a nitrogen–methane mixture is shown in Fig. 6.[26] Data on the thermal diffusion of nitrogen–ethylene mixtures are reported.[15, 27, 38]

Diffusion and Permeation of Nitrogen through Solids

In a recent book which correlates and summarizes diffusion data in condensed phases, Barrer[55] states that diffusion processes are related to chemical kinetics on the one hand and to sorption and solution equilibria on the other. Barrer defines the relationship between permeation and diffusion as follows: in general, there are two states of flow by diffusion: the so-called stationary and non-stationary states. From the former one derives the permeability constant (quantity transferred in unit time per unit area of unit thickness under a standard concentration gradient or pressure difference), and from the latter the diffusion constant. The permeability constant P and the diffusion constant D are related by $P = -D\partial C/\partial X$ where $\partial C/\partial X$

is a standard concentration gradient. One therefore has to deal also with the solubility of the diffusing substance in the solvent. Newitt and Weale point out[56] that Barrer's work confirms the view that permeation is a three-stage process of sorption, diffusion and desorption of the diffusing gas.

SILICA GLASS

Barrer gives the flow of nitrogen through silica glass[55] as an example of the non-specific type of activated diffusion. Experiments were carried out in the range from room temperature to 1000°C. The temperature dependence of the permeation rate, as deduced from the equation $P = P_0 e^{-E/RT}$ is 26,000 g.-cal./mole. Barrer[55] suggests that van der Waals and repulsive forces contribute to the temperature coefficient of flow just as they do to the latent heat of sublimation; in the latter instance the attractive forces, which are small, are predominant, but in the former the much larger repulsive forces are predominant. The mechanism of nitrogen flow through silica glass is thought[50, 55] to result from a structure-sensitive diffusion of the gas down the faults and cracks of molecular dimensions in the silica glass (cf. the structure-insensitive diffusion through the anionic network of the glass itself, corresponding to a solution process; this type of diffusion is exhibited when helium, neon and hydrogen pass through silica glass).

The permeability constant of the nitrogen–silica glass systems is given in Table XLII.[50, 55]

Table XLII.—Permeability Constant of Nitrogen in Silica Glass

Temp., °C.	Permeability Constant × 10^9 (c.c./sec./cm.^{2}/mm./cm. Hg.)		
	A	B	B*
650	0·065	0·066	—
700	0·132	0·146	—
750	0·268	0·271	0·161
800	0·43	0·39	—
850	0·80	0·64	—
900	1·19	0·95	—
950	—	1·44	0·65

Authors: A = Johnson and Burt; B = Barrer; B* = Barrer; decreased permeability due to long heating of silica-glass specimens.

Other work on the diffusion of nitrogen through silica glass and some refractories has been discussed.[58–61, 63]

The diffusion coefficient (cm.^{2}/sec.) of nitrogen in some types of molecular sieve is as follows[62]:

Temp., °C.	Ca mordenite	K mordenite	Ba mordenite
ca. 21	$5{\cdot}0 \times 10^{-15}$	$5{\cdot}5 \times 10^{-14}$	$9{\cdot}3 \times 10^{-12}$
−78	$4{\cdot}3 \times 10^{-18}$	$9{\cdot}2 \times 10^{-16}$	$3{\cdot}1 \times 10^{-14}$
−185		$9{\cdot}2 \times 10^{-20}$	$1{\cdot}4 \times 10^{-17}$

ORGANIC POLYMERS

Barrer[55, 64] has measured the permeation, diffusion and solution of nitrogen and other gases in polymeric organic rubber-like membranes in the temperature range 0° to 100°C. His results are given in Table XLIII. This work was later extended in an investigation of rigid or inelastic membranes of bakelite and ebonite.[55, 65]

Refs. p. 78

Table XLIII.—Permeation of Nitrogen through Polymers

Substance	Temp., °C.	Permeability Constant $P \times 10^6$ c.c. at 293°K./sec./cm.^{2}/mm. thickness/cm. Hg. Pressure
Neoprene	27·1	0·00137
	35·4	0·0023
	44·1	0·0032
	54·1	0·0058
	65·4	0·0106
	84·7	0·0222
Butadiene–methyl methacrylate interpolymer	21·2	0·0028
	44·6	0·0057
	54·0	0·0087
	61·9	0·0132
	77·0	0·023
Polystyrene–butadiene interpolymer	20·0	0·0029
	35·5	0·0057
	50·0	0·0102
	64·2	0·0161
Butadiene–acrylonitrile interpolymer	20·0	0·00061
	38·1	0·0019
	48·5	0·0029
	59·5	0·0048
	70·5	0·0070
	78·6	0·0178
Rubber (vulcanized)	25·0	0·0071
Bakelite	75·0	0·00027
	56·6	0·000115
	47·2	0·000083
	37·5	0·000048
	36·1	0·000047
	20·0	0·0000095
	18·0	0·0000085
Ebonite	67·2	0·000025

The exponential temperature coefficient (E) of the permeability constant in Barrer's equation $P = P_0 e^{-E/RT}$ is given for the previously mentioned organic polymers (see Table XLIII) in Table XLIV.[55, 64, 65]

Table XLIV.—Temperature Coefficient (E) of Permeability Constant of Polymers

Substance	E, g.-cal./mole
'Neoprene' (vulcanized)	10,500
Butadiene acrylonitrile interpolymer	9,800
Butadiene methyl methacrylate interpolymer	9,500
Butadiene polystyrene interpolymer	7,900
Bakelite	10,500

The diffusion constants of the equation $D = D_0e^{-E/RT}$ for various organic polymers are given in Table XLV.

Table XLV.—Diffusion Constants of Organic Polymers

System	Temp., °C.	Diffusion Constants			Ref.
		$D \times 10^5$ cm.^{2}/sec.	D_0 cm.^{2}/sec.	E, g.-cal./mole	
Natural rubber, vulcanized	25 25·3 30 35 40 45 50	0·15 0·121 0·141 0·175 0·212 0·268 0·302		7,400	55, 66
Neoprene, vulcanized	27·1 35·4 44·1 54·1 65·4 84·7	0·019 0·034 0·055 0·096 0·180 0·450	79	11,900	55
Butadiene acrylonitrile interpolymer	17 38·1 48·5 59·5 70·5	0·0066 0·029 0·044 0·088 0·14	28·1	11,500	55
Butadiene methyl methacrylate interpolymer, Sample 1	39·5 55·0 66·0 78·0	0·041 0·092 0·16 0·29	38	11,500	55
Butadiene styrene interpolymer, Sample 2	20·0 35·5 50·0 64·2	0·0237 0·0506 0·095 0·153	0·93	8,900	55

The diffusion data of Newitt and Weale[56] for nitrogen in polystyrene at high pressure are given in Table XLVI and can be expressed by the equation $D = 0{\cdot}21e^{-10{,}000/RT}$.

Table XLVI.—Diffusion of Nitrogen in Polystyrene

Temperature, °C.	Pressure, atm.	$D \times 10^5$, cm.^{2}/sec.
190	270	0·363
181	280	0·213
170	280	0·25
160	282	0·169
149	110	0·11
148	200	0·119
138	272	0·106
120	206	0·052
95	160	0·027
74	205	0·01
18	134	0·0004 approx.

Further diffusion and permeation data for similar organic polymers have been reported.[67–73]

For the diffusion of nitrogen in metals the reader is referred to the appropriate metal in the nitride section of this volume.

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ADSORPTION

Studies of the adsorption of nitrogen on various adsorbents have been made mainly for determining the pore structures of the adsorbent. The reader is referred to a recent review (1957)[1] by Cranston and Inkley which discusses the determination of pore structure from nitrogen adsorption isotherms. There is an increasing tendency to use argon instead of nitrogen in adsorption studies; the former is now readily available and, by virtue of its monatomic nature, it is in some cases preferable to nitrogen.

Adsorption on Silica Gels

A silica gel adsorbent prepared by the hydrolysis of silicon tetrachloride, evacuated at 300°C. and of homogeneous porosity, gave the adsorption figures shown in Table XLVII at −195·7°C. with nitrogen as adsorbate.[2]

Table XLVII.—Adsorption of Nitrogen on Silica Gel at −195·7°C.

ADSORPTION		DESORPTION	
$x=p/p_0$	Nitrogen adsorbed millimols/g.	$x=p/p_0$	Nitrogen absorbed millimols/g.
$1{\cdot}04\times10^{-6}$	$0{\cdot}12_1$	$1{\cdot}20\times10^{-2}$	$3{\cdot}10_0$
$1{\cdot}45\times10^{-5}$	$0{\cdot}54_7$	$2{\cdot}28\times10^{-2}$	$3{\cdot}5_1$
$1{\cdot}35\times10^{-4}$	$1{\cdot}16_8$	$6{\cdot}77\times10^{-2}$	$4{\cdot}1_2$
$1{\cdot}05\times10^{-3}$	$1{\cdot}92_3$	$0{\cdot}129$	$4{\cdot}7_1$
$0{\cdot}58\times10^{-2}$	$2{\cdot}68_6$	$0{\cdot}454$	$7{\cdot}6_7$
$0{\cdot}103$	$4{\cdot}6_7$		
$0{\cdot}383$	$6{\cdot}9_2$		
$0{\cdot}575$	$9{\cdot}2_0$		

p=Partial pressure of Nitrogen; p_0=Saturation pressure of Nitrogen.

From the data given in Table XLVII it is concluded that the Brunauer–Emmett–Teller equation is obeyed for $0{\cdot}035 < x < 0{\cdot}33$; the equation of Harkins and Jura is obeyed for $0{\cdot}075 < x < 0{\cdot}58$; and the monolayer part is not fitted by the equations of Langmuir, Williams or Freundlich.

Examples of the effect of variation in the method of preparation of silica gel and silica–alumina gel on the adsorption properties of these substances are shown in Fig. 7.[3, 4]

The adsorption of nitrogen on silica gel at 0°C. varies almost linearly with pressure.[5]

The heat of adsorption of nitrogen on one type of silica gel was found to be 3000 g.-cal. at 0°C.; this value varied with the method of preparation of the gel.[6]

Refs. p. 93

The total adsorption of an oxygen/nitrogen mixture is always slightly less than the sum of the quantities of the pure gases adsorbed separately at their respective partial pressures.[5] Oxygen is always adsorbed more and nitrogen less than each would be in the absence of the other.[7]

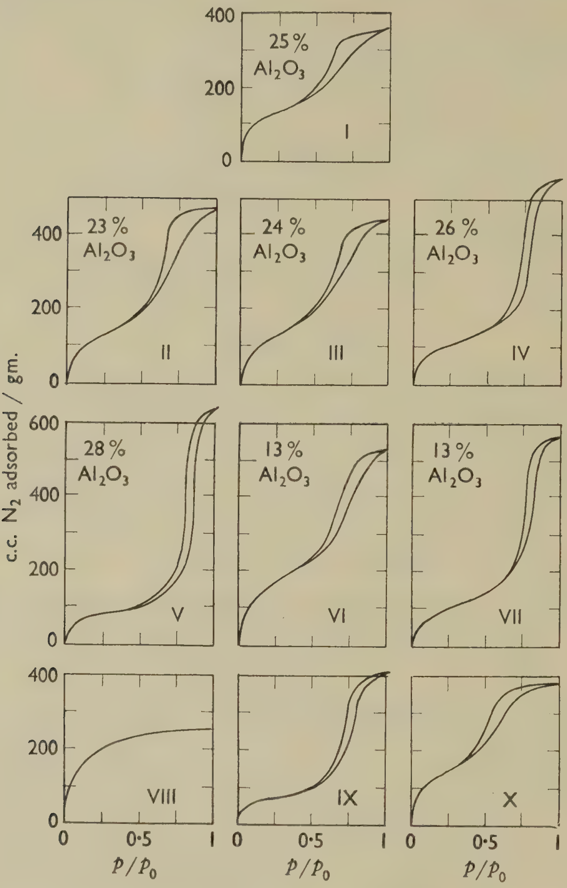

FIG. 7.—Nitrogen absorption–desorption isotherms (−195°C.) for silica gels and silica–alumina gels. (The upper curve in all cases is the desorption curve)

Adsorption isotherms have been obtained for nitrogen/argon mixtures at temperatures from 89·5°K. to 163·0°K. and at pressures between 100 and 700 mm. of mercury.[8]

In a study of the adsorption of nitrogen, hydrogen and their mixtures on silica gel it was found that at 0° and −78°C. nitrogen increased the adsorption of hydrogen and hydrogen decreased the adsorption of nitrogen, whereas at −183°C. nitrogen greatly decreased the adsorption of hydrogen, but hydrogen had almost no effect on the adsorption of nitrogen.[9]

The effect on the nitrogen adsorption–desorption isotherm of wetting the silica gel has been investigated.[10]

Further adsorption data for silica gels, which are mainly of interest in the determination of the surface areas of the adsorbents, have been reported.[11–29]

Adsorption on Glass

Adsorption and desorption isotherms for nitrogen have been measured on various types of porous glass,[28, 30–34, 40] and on powdered glass spheres and plates.[35–43]

The results of Joyner and Emmett[30] for porous glass are given in Fig. 8. From these data the differential heat of desorption was shown to exceed the differential heat of adsorption over the hysteresis region by about 250 g.-cal./mole; this result was correlated with the theory of Brunauer *et al.*

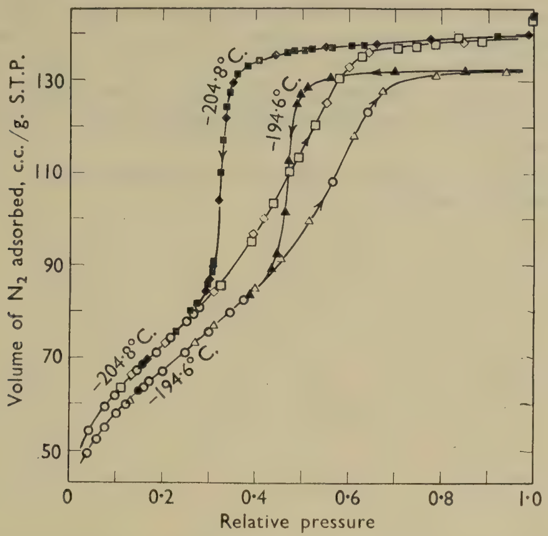

FIG. 8.—Adsorption of nitrogen on porous glass at −204·8°C. and −194·6°C. (Solid symbols are desorption points)

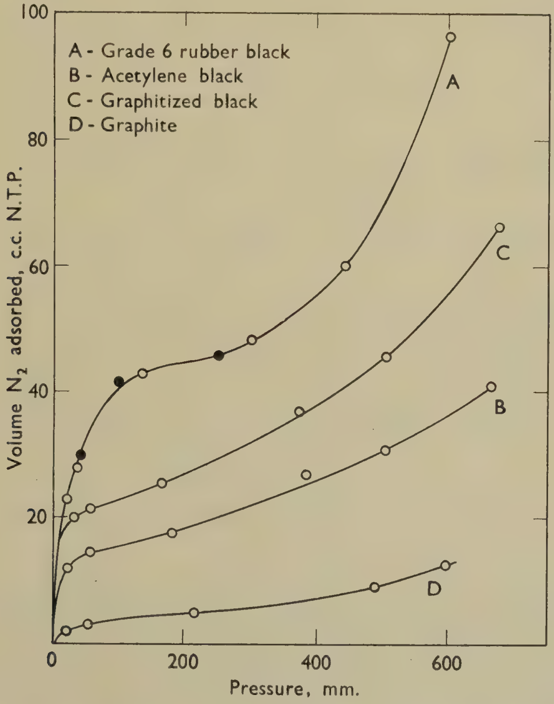

FIG. 9.—Adsorption of nitrogen on carbon blacks and graphite. Isotherms for carbons investigated at −195·8°C.

Adsorption on Carbon

Fig. 9 gives the adsorption isotherms of nitrogen on various carbon blacks at $-195{\cdot}8$°C. up to 600 mm. pressure.[44] Variation in the physical and chemical nature of the carbon black affects this adsorption.[28, 40, 45–57]

From their adsorption isotherms on two carbon black samples, Joyner and Emmett have determined the differential heats of adsorption of nitrogen on carbon blacks at temperatures ranging from -183°C. to -205°C.; the values range from 1·5 to 3·5 kcal./mole. The changes in free energy and entropy for the process of change from liquid nitrogen to adsorbed nitrogen were also calculated as a function of the surface covered.[45]

Partial graphitization of carbon black by heat treatment alters considerably the shape of the adsorption isotherm.[46]

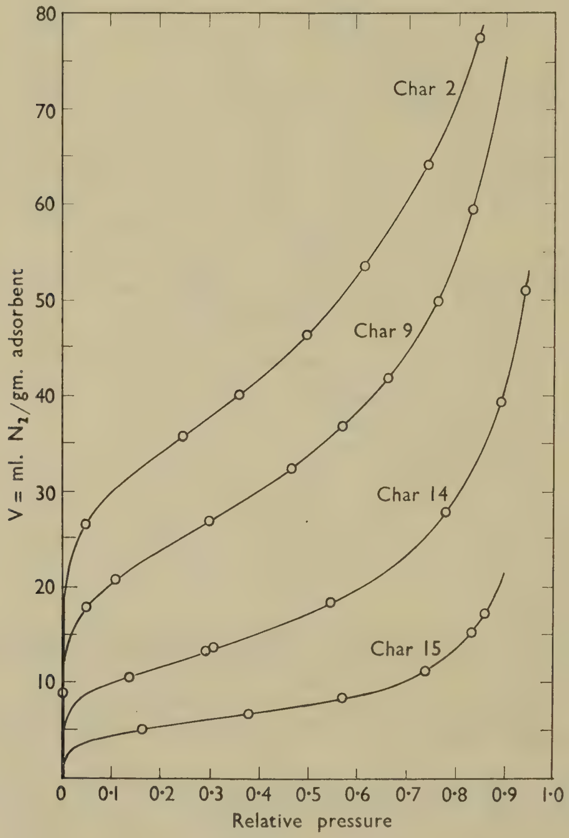

FIG. 10.—Adsorption of nitrogen on adsorbent carbons at 77°K.

From isotherm measurements for the system nitrogen on Graphon, the complete set of thermodynamic functions has been calculated. The extreme sensitivity of calculations to errors in measurements of low pressures indicated the need for further refinements in experimental techniques.[47]

A considerable amount of research has been carried out on the adsorption of nitrogen on various types of activated carbons and charcoals.[21–23, 27, 40–42, 55, 57–83]

In these studies, adsorption has been determined over wide ranges of temperature (from ca. -180°C. to ca. $+200$°C.) and of pressure (up to ca. 400 atm.)

The effects of various combinations of steaming, hydrogenation, oxidizing, sintering or impregnating with nickel oxide, copper oxide, molybdenum oxide, sodium carbonate, ferric oxide or chromium sesquioxide on the adsorptive properties of charcoals have been studied.[59]

Examples of the isotherms obtained for different types of activated carbons and charcoals are given in Figs. 10–15,[66] where v = volume nitrogen adsorbed in ml./g. adsorbent; relative pressure = (P/P_0) = (equilibrium pressure over adsorbent)/(saturation pressure of liquefied gas at temperature T).

The differential and integral heats of adsorption of nitrogen on various activated charcoals have been determined.[42, 75–77]

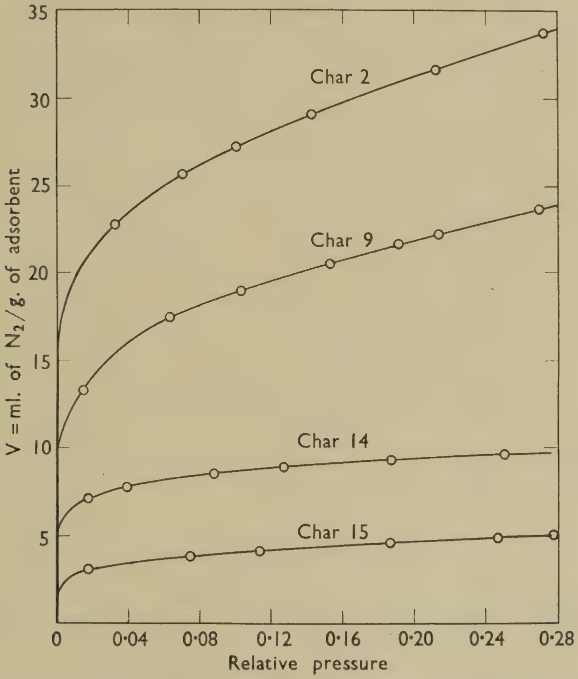

FIG. 11.—Adsorption of nitrogen on adsorbent carbons at 90°K.

Calculation of entropy changes on adsorption as a function of surface coverage shows agreement with the mobile adsorption model between 0°C. and −80°C. with no loss of freedom of rotation in the two-dimensional layer. At higher temperatures, the adsorbed nitrogen molecules show vibration with respect to the surface and have a certain degree of supermobility. Down to 84°K. and at high degrees of coverage there is a restriction in free translation, but the rotation of the nitrogen molecule is not hindered.[82]

The adsorption from mixtures of argon and nitrogen at 22° and −78°C. by charcoal follows Dalton's Law, but at −183°C. the adsorption from the mixture is less than that calculated for the sum of the simple components.[60]

The adsorption on charcoal of nitrogen/hydrogen[72, 83] and nitrogen/oxygen and nitrogen/carbon dioxide[82] mixtures is reported.

Other carbonaceous adsorbents which have been investigated are graphite[44, 84–92] (see Fig. 9), diamond,[89, 92] coal[93–96] and carbide powders.[92]

The heat of sorption[85] of nitrogen on graphite in the temperature range 273° to 79°K. does not depend on the temperature, but it is a function of the quantity adsorbed; the initial heat is 4600 g.-cal./mole and the limiting heat is 2500 g.-cal./mole. Barrer[85] considers that the initial heat is due to adsorption in the cracks of the adsorbent, and the limiting value results from sorption on a plane surface.

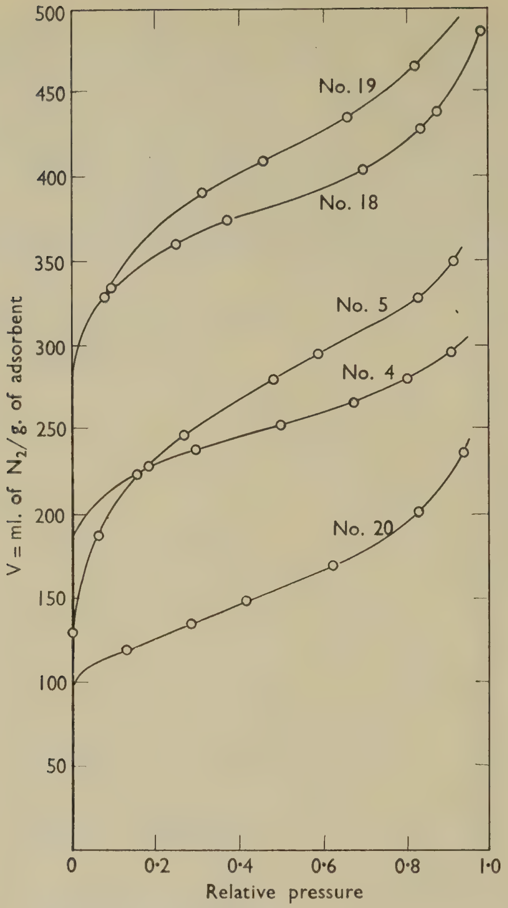

FIG. 12.—Adsorption of nitrogen on adsorbent carbons at 77°K.

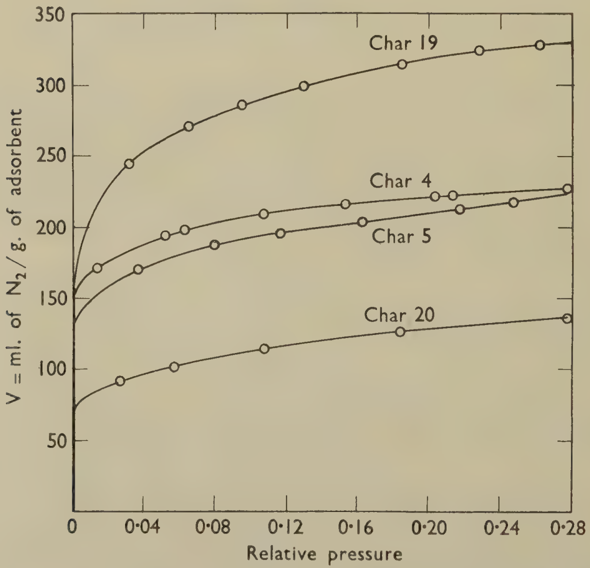

FIG. 13.—Adsorption of nitrogen on adsorbent carbons at 90°K.

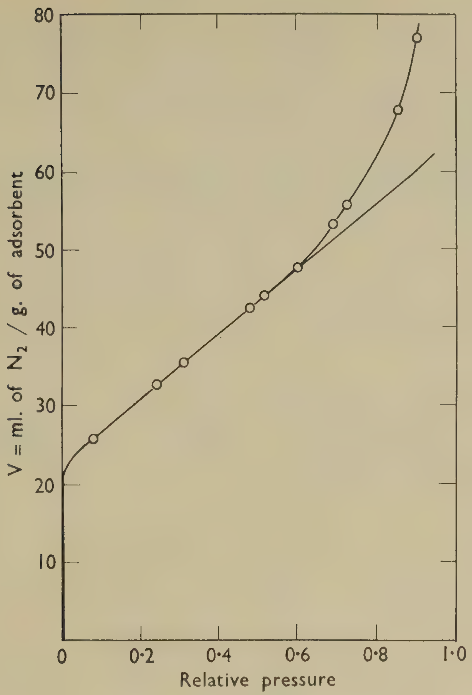

FIG. 14.—Adsorption of nitrogen on adsorbent carbons at 77°K.

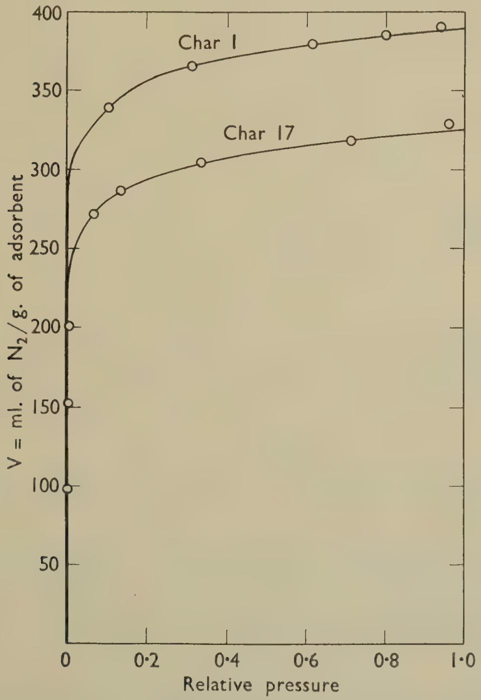

FIG. 15.—Adsorption of nitrogen on adsorbent carbons at 77°K.

Adsorption on Minerals

Adsorption studies on the following minerals have been reported: attapulgite,[97, 98] molecular sieves and zeolites (e.g. gmelinite, mordenite and chabazite),[34, 99–106] montmorillonite,[107–111] Fuller's earth,[112] clays,[113, 114] bentonites,[115, 116] gibbsite,[117] dehydrated gypsum,[118] mica,[39] aluminium silicates[21] and Portland cements,[119] plaster of Paris[134] and marble.[134]

Unlike other adsorbents the so-called 'Linde Molecular Sieves'[206] have rather unusual selectivity which is determined by the size and other characteristics of the molecule to be adsorbed. Only those molecules that are small enough to pass through the pores of the crystal can enter the cavities and be adsorbed on the interior surface. This sieving or screening action, combined with their adsorptive attraction, makes it possible for molecular sieves to separate molecules which are smaller than the size of the pores from those that are larger.

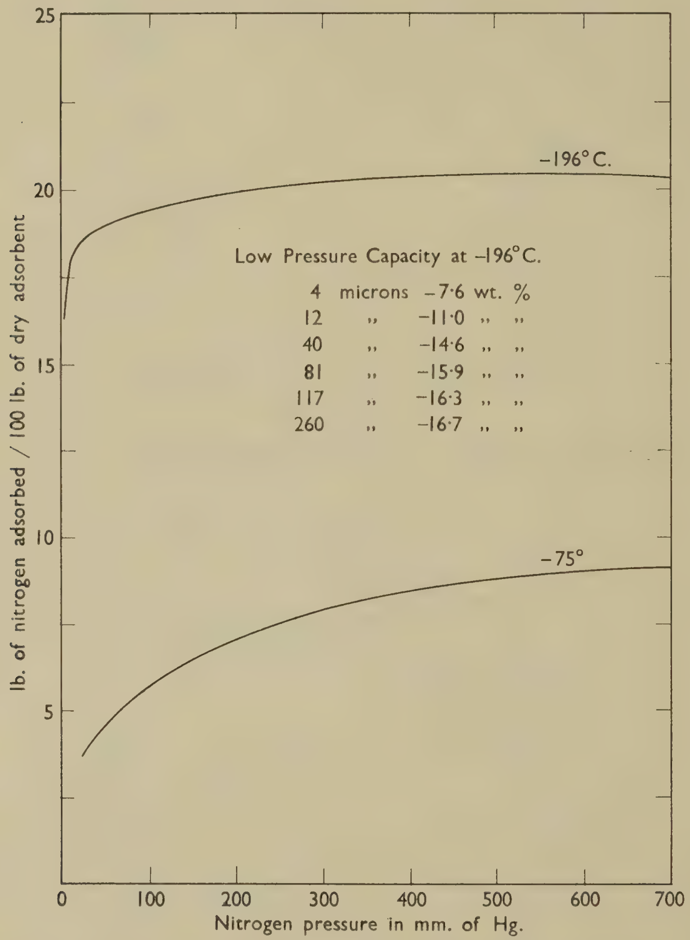

FIG. 16.—Nitrogen adsorption isotherms: Union Carbide molecular sieves type 5A. pellets

In the investigation of molecular sieves it was found that the behaviour of these substances can be extended considerably by sorbing at low temperatures (−183° to −195°C.) those gases that have a small energy of activation for diffusion. In this way by using a suitable molecular sieve adsorbent, differences in the sorption rates of nitrogen, oxygen and argon were found which seemed to permit quantitative or semi-quantitative resolution of their mixtures; the rates found were in the expected order: oxygen, nitrogen, argon, krypton.[104, 105]

Fig. 16 gives the adsorption isotherms of nitrogen on Union Carbide Molecular Sieves, type 5A[206] at temperatures of −75°C. to −196°C. (Type 5A refers to the size of pore openings—molecules up to about 5 A. in diameter being able to enter the pores; the curves are based, with permission, on data supplied by the Union Carbide Corporation.)

In a study of the adsorption of a hydrogen/nitrogen mixture on mordenite at −183°C., no evidence of enhancement of adsorption was obtained although mutual interference effects were observed.[99]

The nitrogen adsorption properties of pure chabazite crystals, after ionic exchange with sodium chloride, potassium chloride, barium chloride, tin chloride and calcium chloride, have been determined.[100]

The calculated initial heat of adsorption of nitrogen on chabazite in the temperature range 62°K. to 384°K. is 8800 g.-cal./mole; this is reported to be the largest van der Waals interaction energy for nitrogen.[102] As with graphite the differential heat decreased at first with the amount of gas adsorbed, then reached an apparent limiting value.[215]

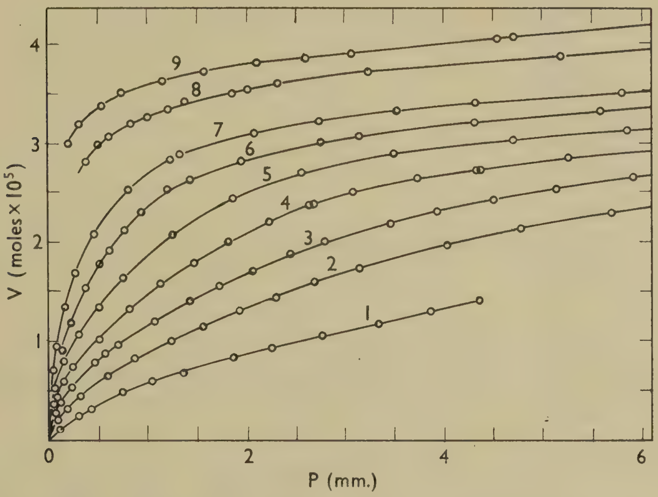

FIG. 17.—Adsorption of nitrogen on cæsium iodide at various temperatures (1, 87·58; 2, 83·56; 3, 81·55; 4, 79·52; 5, 77·49; 6, 75·50; 7, 73·50; 8, 69·50; 9, 65·54°K.)

Adsorption on Salts, etc.

Data for the adsorption of nitrogen on the following salts have been determined: sodium chloride,[120–123] sodium nitrate,[122] potassium chloride,[124, 125] caesium iodide,[125–127] copper sulphate,[23] calcium fluoride,[128] cadmium bromide,[86] cadmium chloride,[86, 122] cadmium iodide,[86] lead chloride,[129, 130] ammonium phosphomolybdate,[131] molybdenum disulphide,[86] potassium permanganate.[132, 133]

The isotherms obtained for the adsorption of nitrogen on cæsium iodide[127] between 65·5° and 87·6°K. are shown in Fig. 17.

The adsorption of a nitrogen/carbon monoxide mixture at 83·6°K. by cæsium iodide follows a 'mixed' Langmuir equation.[126]

Adsorption on Metal Oxides

Adsorption characteristics for nitrogen on the following metal oxides are reported: copper oxide,[134] magnesium oxide,[64, 135–137] zinc oxide,[24, 25, 28, 135] cadmium oxide,[135, 138] aluminium oxide[25, 27–29, 134, 139] (including hydrated alumina, heated alumina gels, molybdena-impregnated alumina, dehydrocyclization catalysts, and fresh and coked silica–alumina cracking catalysts), ferric oxide,[52, 134, 140–144] stannic oxide,[24] titanium dioxide (rutile and anatase),[24, 52, 145–157] chromium sesquioxide,[135, 158–162] nickel oxide.[142]

The adsorption isotherms of nitrogen on rutile at 77° and 91°K. are shown in Fig. 18.[145]

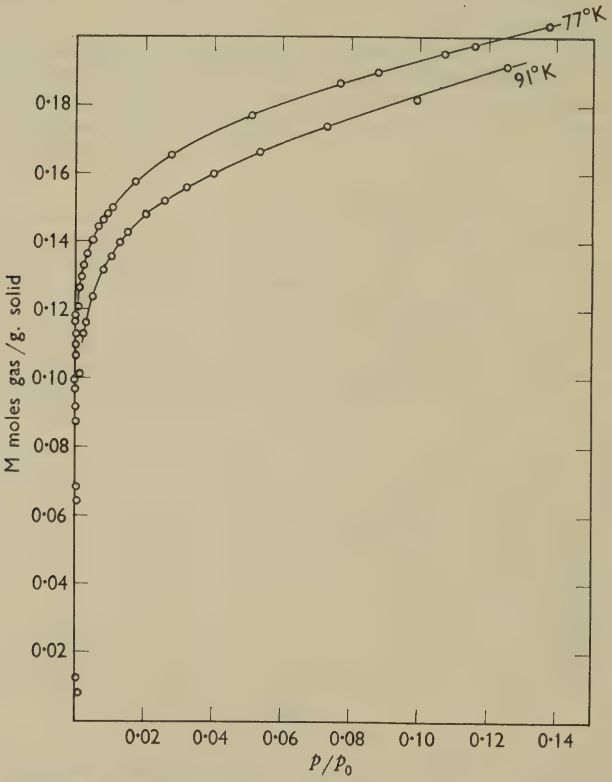

FIG. 18.—Adsorption isotherms of nitrogen on rutile

The thermodynamic properties and heat of adsorption of nitrogen on rutile[150, 153] and anatase[151] have been determined. The magnitude of the heat of adsorption on anatase indicates that the adsorption is of van der Waals type.[151]

In adsorption studies for nitrogen/oxygen mixtures at 78·2°K. on Harkins' anatase it was shown that selective adsorption of nitrogen occurs on this surface at low coverage. Comparison with the extended Brunauer–Emmett–Teller theory shows qualitative disagreement and provides evidence against at least one of the assumptions of this theory. Use of a 'liquid entropy' model gives semi-quantitative agreement with experiment. This model allows the prediction of mixed adsorption behaviour from pure gas isotherms for pairs of gases for which Raoult's law holds approximately.[155]

Fig. 19 shows some of the results obtained for the adsorption of nitrogen at −195°C. on chromium oxide gel.[158]

It was observed that chemisorption of small quantities of hydogen had substantially no effect on the physical adsorption of hydrogen at −195° and −78°C. and of nitrogen at 0°C.

The van der Waals heat of adsorption of nitrogen on chromium oxide at −183°C. is about 4 kcal./mole and the heat of activated adsorption also at −183°C. is about 8 kcal./mole; the latter figure of 8 kcal./mole is extremely small if it does really represent chemisorption.[215]

In the adsorption of oxygen–nitrogen mixtures on chromium oxide at −185·6°C. the total gas adsorbed tends to agree with Hill's equation.[159]

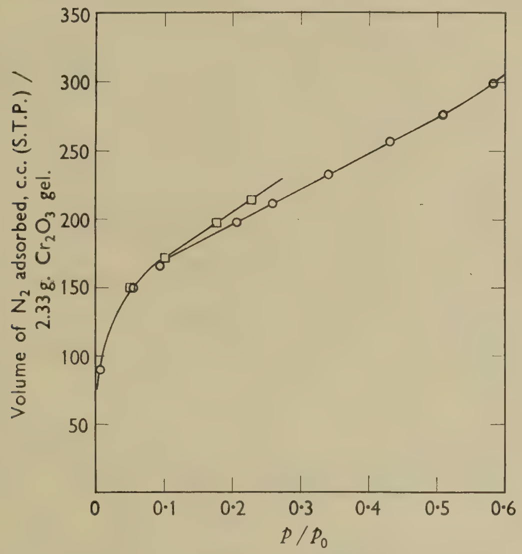

FIG. 19.—Adsorption of nitrogen on chromium oxide gel

○ = N_2 adsorption before hydrogen chemisorption
□ = N_2 adsorption at −195° after chemisorption of 8·3 c.c. of hydrogen at 150°

Adsorption on Metals

Studies of the adsorption of nitrogen on the following metals have been made: magnesium,[163, 164, 178] calcium,[163, 250] cadmium,[250] copper[165–171, 250] (including basic magnesium carbonate as a promoter on a copper surface[170]), silver,[25, 35, 36, 172, 250] gold,[250] zinc,[173, 250] mercury,[174] barium,[175–178, 250] aluminium,[250] indium,[250] nickel,[179–183, 250] cobalt (and cobalt catalysts),[184–186] tin,[250] molybdenum,[187, 188, 250] lead,[250] titanium,[189, 250] zirconium,[189, 190, 230, 250] tungsten,[25, 28, 191–198, 250] platinum,[197, 199–202, 250] palladium,[203, 250] rhenium,[250] tantalum,[204, 250] chromium,[205] iron and iron catalysts—see below.

Fig. 20 shows the type of adsorption isotherm exhibited by silver at −183°C. and −195°C. which can be presented satisfactorily by the Langmuir equation.[172]

A considerable amount of research on the adsorption of nitrogen on iron has been undertaken because of the importance of this metal as a catalyst in the manufacture of ammonia from synthesis gas[207–247]; these data also include work carried out on different types of promoted iron catalysts.

Examples of the type of isotherm obtained for various iron and promoted iron catalysts are given in Fig. 21.[237]

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Isotherms obtained by Emmett and Brunauer[214] at 400°C. and 500°C. indicate that the heat of chemisorption of nitrogen on iron is about 35 kcal./mole for an adsorption of 0·010 to 0·014 c.c. of nitrogen per g. of iron. Brunauer[215] points out that the heat of chemisorption approximates to the heat of formation of iron nitrides. From calorimetric experiments, Beebe and Stevens[224] estimate that the heats of van der Waals adsorption range from 2·5 to 4·4 kcal./mole at −183°C.

The activation energy for the chemisorption of nitrogen on iron varies linearly (10–30 kcal./mole) with the coverage[243]; a mean value of 16–17 kcal./mole had been determined in earlier work by Emmett and Brunauer.[214]

It is reported that the measured heats of adsorption of a mixture of nitrogen and hydrogen on an iron catalyst indicate that in the ammonia synthesis the surface is covered with nitrogen to the extent of 99·99996%. Aside from the possible reaction of hydrogen from the gas phase, three alternative explanations are advanced to account for the occurrence of the ammonia reaction which ensues in spite of the apparent lack of room for hydrogen on the surface:

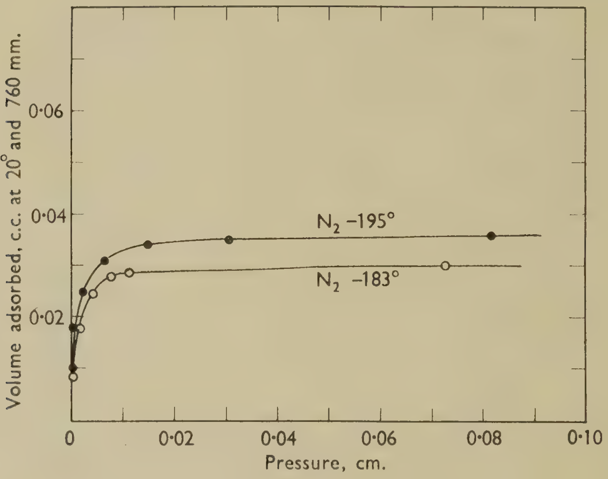

FIG. 20.—Adsorption of Nitrogen on Silver

(1) adsorption of nitrogen and hydrogen on different crystallographic sites;
(2) solution of hydrogen in the metal; and
(3) decrease in the heats of adsorption with increasing coverage of the surface in such a way as to bring the values for nitrogen and hydrogen closer together.

The adsorption of nitrogen on various steels is reported.[248, 249] The adsorption of nitrogen on cold-rolled steel was determined at 20°, −78°, −183° and −195°C. and at pressures up to 0·1 cm. A unimolecular layer of physically held nitrogen was sorbed on an unreduced surface at −183°C., but approximately 15% of the total volume of gas sorbed was held so strongly that it could not be desorbed by reducing the pressure at that temperature. A similar monolayer of physically held nitrogen was adsorbed on a reduced surface, but could be entirely desorbed by evacuation of the system at the same temperature. The ordinary analogue of the Clausius–Clapeyron equation does not in principle yield a correct value for the heat of adsorption; the Emmett–Brunauer–Teller equation appears to be preferable. The heat of adsorption calculated by this method is approximately 3 kcal./mole; it is influenced more by the physical nature of the surface than by the chemical nature of the gas. The isotherms are represented in the low pressure range by the Freundlich equation

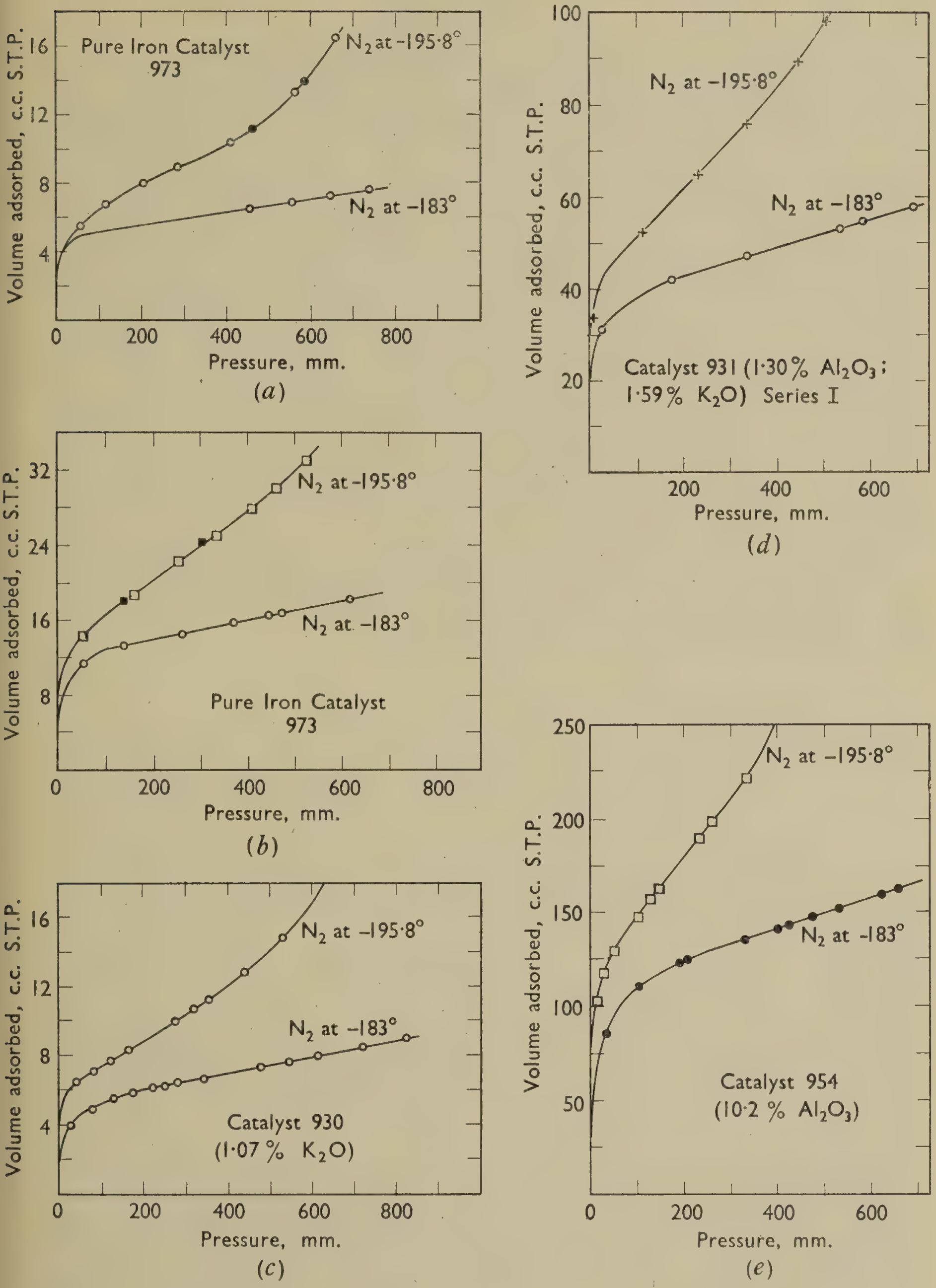

FIG. 21.—Adsorption of Nitrogen on Iron and Promoted Iron Catalysts

and in the high pressure range by the Langmuir relation. A combination of these equations,

$$v = v_s \sqrt[n]{ap/(1+ap)}$$

represents most of the results over the whole range of pressure.[248]

In a recent study of gas chemisorption, Trapnell[250] (see also references 251 and 252) discusses the interaction of nitrogen and other gases with clean evaporated films of some twenty metals, at temperatures from 0 to -183°C. The order of affinity of these gases in chemisorption is oxygen > acetylene > ethylene > carbon monoxide > hydrogen > nitrogen. The following metals: tungsten, tantalum, molybdenum, titanium, zirconium, iron, calcium and barium chemisorbed nitrogen, but nickel, palladium, rhenium, platinum, copper, aluminium, zinc, cadmium, indium, tin, lead, silver and gold did not. Chemisorption occurred instantaneously and irreversibly at room temperatures with the metals tungsten, tantalum, molybdenum, titanium, zirconium and barium. In the case of iron normal chemisorption with complete breakage of the $N \equiv N$ bond takes place at a measurable rate only at room temperatures and above, whilst at -183°C. there is rapid but weak chemisorption which probably does not completely break the $N \equiv N$ bond.

Porter and Tompkins[234] have reached similar conclusions, heats of adsorption of 5·2 and 3·1 kcal./mole being obtained for nitrogen adsorption values of 0·083 and 0·097 millimole/g. iron respectively (at 78°K.); these results correspond to molecular adsorption at 78°K. At 273°K. the heat of adsorption is about 40 kcal./mole, corresponding to chemisorption.

In the case of calcium (which might have been contaminated) chemisorption was activated, and between -78°C. and room temperatures the velocities were measurable. The activation energy was observed to increase with increasing adsorption and values of 1500 and 3800 g.-cal. were recorded.

EFFECT OF THE METAL *d*-BAND

Trapnell analyses these results in relation to the so-called *d*-band theory which postulates that the chemical bond between metal and adsorbate involves the metal *d* band. (The best metal catalysts for a variety of reactions are the transition metals or the near transition metals of Group 1B of the periodic table, a fact that gave rise to the *d* band theory.) With barium and calcium it is possible that the uptake of nitrogen is nearer to nitride formation than to pure chemisorption; *s* electrons may be operating rather than those in the *d* band. It is interesting to note that some transition metals, e.g. nickel, do not chemisorb nitrogen; hence it seems that the presence of *d* band vacancies is not a sufficient condition for chemisorption of simple gases. Trapnell considers that with nitrogen three vacancies or more in the shell of the isolated metal atom are required for chemisorption as atoms at room temperatures or below. Iron with three vacancies is just active, whereas rhenium which has two vacancies and nickel, palladium and platinum which have a single vacancy are inactive. Owing to the higher valency of the nitrogen atom, more extensive *d* band vacancies are required for nitrogen chemisorption then for chemisorption of other gases.

Measurements of the chemisorption of nitrogen on tungsten powder over the pressure range 10^{-6} to 35 mm. and at temperatures between 400° and 750°C. show that at saturation one molecule of nitrogen is adsorbed for every four tungsten atoms on the surface. The heat of adsorption is constant at about 75·0 kcal./mole in the low-coverage range and decreases according to the relation $Q = 139{\cdot}0 \log s/A$ (kcal./mole) in the higher-coverage range. The energy of activation is approximately 10.0 to 25·0 kcal./mole and varies with the surface covering.[191]

In the adsorption of nitrogen by binary alloys such as iron–chromium and iron–manganese it was found that nitrogen atoms have a tendency to cluster around chromium or manganese atoms.[253]

Nitrogen tends to stabilize silver sols which are on the borderline of stability; there is, however, no increase in the average charge of the particles.[254]

Miscellaneous Aspects

The adsorption of nitrogen on hexamethylenetetramine,[255] polyethylene, nylon and collagen at liquid nitrogen and liquid oxygen temperatures shows typical behaviour designated Type II by Brunauer, Emmett and Teller, except for a rather gradual break where the monolayer is completed.[256] Polystyrene has also been investigated.[88]

Wool and viscose rayon are reported to have slightly greater adsorptive capacities for nitrogen than has silk or cotton.[257]

Adsorption studies on several samples of dry lyophilized protein show that non-polar gases such as nitrogen are physically adsorbed by the proteins in a manner that is independent of the specific protein and depends principally on the state of sub-division.[258]

The effect of the adsorption of nitrogen on the resistance of semi-conducting films composed of Cu_2O–CuO has been studied. Nitrogen, like oxygen, decreases the resistance whereas hydrogen and carbon monoxide increase the resistance of the film on adsorption.[259]

By considering the adsorbate (nitrogen) as a highly compressed gas, its volume and fugacity can be calculated by the Lewis modification of the Polanyi–Dubinin equation. This method has been applied satisfactorily to the adsorption of nitrogen on activated charcoal, silica gel and activated alumina both above and below the critical temperature. On further modification, the equation has been applied also to predicting the adsorption of oxygen/nitrogen mixtures on activated carbon.[260]

By using a value of 15·4 sq. A./mol. for the cross-sectional area of the nitrogen molecule adsorbed at −196°C., it was possible to calculate from adsorption data the cross-sectional areas for other molecules; it was shown that these calculated areas agree with those predicted for the molecules on the basis of measurement of liquid density or van der Waals constants. This agreement would have been less satisfactory if the conventional value of 16·2 sq. A./mol. had been taken for the nitrogen cross-sectional area.[261]

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SOLUBILITY OF NITROGEN

Solubility of Nitrogen in Water

The solubility of nitrogen in water has been measured by Morrison and Billet[1–3] at 1 atm. pressure. The values they obtained for the absorption coefficient, S_0, (c.c. at N.T.P./1000 g. water) at a total gas pressure of 1 atm. are given in Table XLVIII.

Table XLVIII.—Solubility of Nitrogen in Water at 1 *Atmosphere*

t°C.	12·5	15·5	20·3	25·5	30·0	35·6	41·6	46·4	51·0	55·5	63·8	72·5
S_0	18·37	17·22	15·89	14·76	13·77	12·74	11·97	11·53	11·25	11·07	10·72	10·54

Table XLIX gives the solubility of nitrogen in water at different temperatures and pressures as determined by other workers. (See also the graph given by Frohlich *et al.*[4])

Table XLIX.—Solubility of Nitrogen in Water (cc. N_2 (N.T.P.)/g. of Water) at different Temperatures and Pressures

Temp., °C.	Pressure, Atmospheres	Goodman and Krase[5]	Wiebe, Gaddy and Heins[6]	Wiebe, Gaddy and Heins[7]	Saddington and Krase[8]	Pray, Schweickert and Minnich[9]
0	100	1·46				
	125	1·76				
	200	3·19				
	300	3·60				
25	25		0·348	0·348		
	50		0·674	0·674		
	100	1·07	1·265	1·264		
	125	1·44				
	200	2·76	2·257	2·257		
	300	3·25	3·057	3·061		
	500		4·436	4·441		
	800		6·13	6·134		
	1000		7·14	7·15		
50	25			0·273		
	50			0·533		
	100	1·003		1·011		
	125	1·24				
	200	2·49		1·830	1·806	
	300	2·99		2·534	2·572	
	500			3·720		
	800			5·221		
	1000			6·123		
65	100				0·981	
70	300				2·425	
75	25			0·254		
	50			0·494		
	100			0·946		
	200			1·732		
	300			2·413		
	500			3·583		
	800			5·062		
	1000			5·934		
80	100	0·934			0·977	
	125	1·15				
	200	2·27			1·748	
	300	2·86				
100	25			0·266		
	50			0·516		
	100	0·954		0·986		
	125	1·17				
	200	2·25		1·822	1·825	
	300	2·91		2·546		
	500			3·799		
	800			5·365		
	1000			6·256		
105	300				2·598	
125	100				1·198	

Continued overleaf

Temp., °C.	Pressure, Atmospheres	Goodman and Krase[5]	Wiebe, Gaddy and Heins[6]	Weibe, Gaddy and Heins[7]	Saddington and Krase[8]	Pray, Schweickert and Minnich[9]
135	300				3·128	
144	100	1·025				
	125	1·30				
	200	2·68				
	300	3·46				
150	200				2·172	
165	300				3·905	
169	100	1·08				
	125	1·52				
	200	3·29				
	300	3·83				
180	100				1·644	
200	200				3·287	
210	100				1·817	
230	300				6·062	
240	100				2·027	
240	200				4·378	
260	10·2					0·44
	27·2					1·24
315·5	10·2					0·55
	20·4					1·56
	27·2					2·32

Pray, Schweickert and Minnich[9] have plotted some of the data with their own results (Fig. 22); it is evident that there is a minimum in the isobars at about 190°F. Work at high pressure has been carried out by Basset and Dodé[10] who have determined the solubility of nitrogen in water at 18°C. over the pressure range 500 to 4500 atm., with the results given in Table L.

Table L.—Solubility of Nitrogen in Water at 18°*C. and at Different Pressures*

Pressure, kg./sq. cm.	500	1000	2000	3000	4000	4500
c.c. N_2/g. H_2O (N.T.P.)	4·3	6·1	6·9	7·0	6·4	6·0

The authors remark that the nitrogen used had a purity of 99·7% but unavoidably contained traces of oil, which perhaps explains the differences from the results of Wiebe *et al.*[6, 7] in the 500 to 1000 atm. range. It will be noted that the solubility rises to a maximum at about 3000 atmospheres.

By means of their own equation:

$$-\log f_2/N_2 = \log K + \bar{V}_2P/2{\cdot}303\,RT$$

(where f_2 = fugacity of nitrogen;
N_2 = mole fraction of gas in solution;
K = Henry's coefficient;
$\bar{V}_2$ = partial molal volume of the dissolved nitrogen;
P = total pressure)

Krichevsky and Kazarnovsky[11] calculated theoretically solubilities of nitrogen, which were in good agreement with the results of Wiebe *et al.*[6, 7] Despite the fact that they considered Basset and Dodé's results not particularly accurate, Krichevsky and Kazarnovsky[12] were able to determine the existence of a maximum from their equation. At the maximum $(\partial \ln N_2/\partial P) = 0$ and hence $\bar{V}_2 = 32{\cdot}7$ c.c., which agrees with the value obtained by the extrapolation of Amagat's compressibility data to 18°C. and 3000 kg./sq. cm.

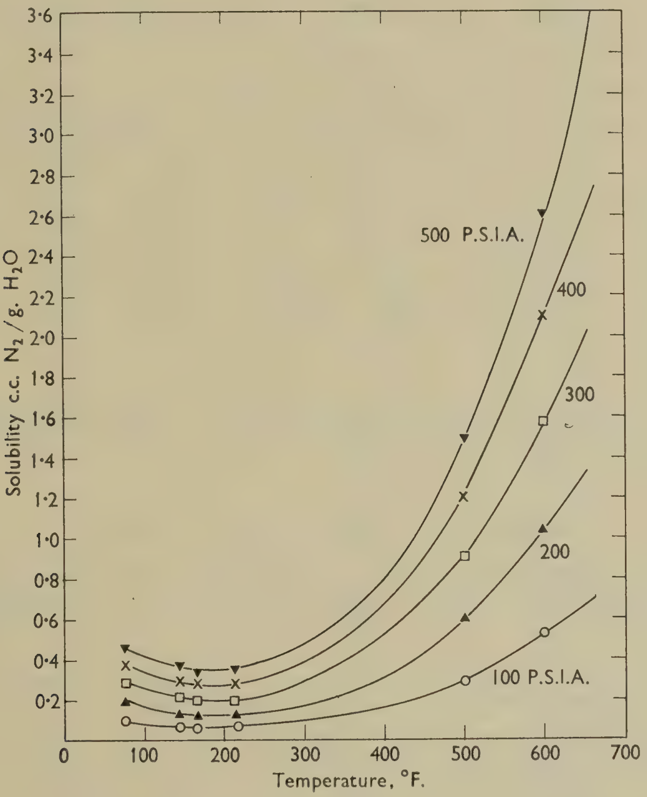

FIG. 22.—Solubility of nitrogen in water at varying temperatures[9]

Partial molal volumes of nitrogen dissolved in water have been calculated by Krichevsky and Il'inskaya,[13] and also by Gonikberg using a modification of the Krichevsky and Kazarnovsky equation.[14]

Investigations have been carried out on the solubility of nitrogen in solutions of sodium sulphate,[15] sodium chloride,[3, 18] sodium carbonate,[16] sodium bicarbonate,[16] potassium chloride,[3, 17] potassium iodide,[3] lithium chloride,[3] lanthanum chloride,[3] barium chloride,[3, 18] hydrogen chloride[3, 16] and urea[18]; in addition, the effect of temperature and pressure variation on the solubility in potassium chloride solution is reported.[17]

The solubility of nitrogen in sea water has received further attention[19] (cf. Mellor, VIII, 76).

Refs. p. 118

Solubility of Nitrogen–Hydrogen Mixtures in Water

The solubility of a 3:1 hydrogen–nitrogen mixture in water was determined at 25°C. and at pressures from 50 to 1000 atm. by Wiebe and Gaddy[20] (Table LI). Calculation by the same authors of this solubility from the solubilities of the pure constituents gave results deviating by as much as 13% at 800–1000 atm. Kielland[21] has shown that better agreement can be obtained (see Table LI) if the calculated values are corrected with the activity data given by Merz and Whittaker. The assumption thus made is similar to that of Krichevsky and Kazarnovsky[22] whose equation, when applied to the solubility of nitrogen–hydrogen mixtures in water, also gives reasonable agreement with experimental results.

Table LI.—Solubility of a 3:1 *Hydrogen–Nitrogen Mixture in Water at* 25°*C.*

(Solubility expressed as c.c. of gas at N.T.P. per g. of water.)

Pressure, atm.	Observed (Wiebe and Gaddy[20])			Calculated (Kielland[21])		
	H_2	N_2	Total	H_2	N_2	Total
50	0·6694	0·1655	0·8349	0·663	0·161	0·824
100	1·328	0·315	1·643	1·321	0·307	1·628
200	2·652	0·557	3·209	2·591	0·563	3·154
400	5·118	0·950	6·068	5·046	0·983	6·029
600	7·482	1·327	8·809	7·394	1·332	8·726
800	9·665	1·662	11·327	9·617	1·625	11·24
1000	11·778	1·946	13·724	11·78	1·89	13·67

The solubility of nitrogen–carbon dioxide mixtures in water has been investigated by Zel'venskii[23, 24] at 25°C. and at pressures from 25 to 300 atm.

Solubility of Nitrogen in Organic Solvents

From an investigation of the solubility of nitrogen in ethanol, propanol, butane, heavy naphtha, gas oil and carbon tetrachloride at 25°C. and at pressures up to 200 atm., Frolich *et al.*[4] showed that Henry's law was obeyed over a wide pressure range.

Values of the Ostwald absorption coefficient, γ, of nitrogen in different solvents at various temperatures (Tables LII and LIII, respectively) have been reported by Horiuti[25] and by Kretschmer, Nowakowska and Wiebe.[26]

Gjaldbaek and Hildebrand[27] have reported values of the Bunsen absorption coefficient for the solubility of nitrogen in some organic liquids. Their results, given in Table LIV, show that the order of solubility, expressed as mole fraction, closely parallels the order of the solubility parameters, defined as the square root of the energy of vaporization per c.c.

The solubility of nitrogen in various organic polymers is given in Table LV.[28,29]

Gjaldbaek and Hildebrand[30] have shown that the values for the partial molal volume of nitrogen in organic solutions (see Refs. 25 and 27) increase markedly with decreasing internal pressures of the solvents.

The solubility of nitrogen in methanol (c.c. at N.T.P. in 1 g.) at 0°C. is 7·7 and 28·5 at 48·4 and 194 atm., respectively.[31]

The solubility of nitrogen in fats and oils is reported.[32, 33] Ipatieff and Levina[34] have investigated the solubility of nitrogen and other gases in shale gasoline and in kerosine at various pressures and temperatures. Burrows and Preece[35] and Hildebrand[36] have discussed theoretically the solubility of nitrogen in non-electrolytes.

Table LII.—Solubility of Nitrogen in Organic Solvents (*Horiuti*)

γ = Ostwald Absorption Coefficient

Solvent	Temperature, °C.	γ (observed)
Carbon tetrachloride	60·1	0·1953
	40·1	0·1754
	20·0	0·1572
	0·0	0·1403
	−19·7	0·1256
Chlorobenzene	80·3	0·1399
	60·05	0·1259
	40·1	0·1116
	20·0	0·0994
	0·0	0·0881
	−19·7	0·0778
	−39·7	0·0695
Benzene	60·0	0·1575
	40·0	0·1355
	20·0	0·1162
	7·1	0·1063
Acetone	41·1	0·1946
	20·0	0·1747
	0·0	0·1553
	−20·2	0·1376
	−40·75	0·1211
	−60·3	0·1081
	−78·1	0·0967
Methyl acetate	40·1	0·1957
	20·0	0·1748
	0·0	0·1551
	−20·3	0·1353
	−40·6	0·1190
	−60·1	0·1032
	−78·7	0·0900
Ethyl ether	20·0	0·2870
	0·0	0·2672
	−20·5	0·245
	−41·1	0·2286
	−60·6	0·2144
	−77·7	0·2055

Table LIII.—Solubility of Nitrogen in Organic Solvents (Kretschmer, Nowakowska and Wiebe)

γ = Ostwald Absorption Coefficient

Solvent	Temperature, °C.	γ (observed)
Ethanol	−25	0·1280
	0	0·1391
	25	0·1489
	50	0·1606
Ethanol + Water (95% Ethanol by volume)	−25	0·0944
	0	0·1053
	25	0·1160
	50	0·1290
Methanol	−25	0·1435
	0	0·1532
	25	0·1645
	50	0·1765
iso-Propanol	0	0·1353
	25	0·1465
	50	0·1617
Butanol	0	0·1075
	25	0·1225
	50	0·1358
Acetone	−25	0·1340
	0	0·1554
	25	0·1816
iso-Octane	−25	0·1943
	0	0·2088
	25	0·2258
	50	0·2452
Acetone + Ethanol (50% by volume)	0	0·1427
	25	0·1609
	50	0·1829
iso-Octane + Ethanol (50% by volume)	0	0·1785
	25	0·1939
	50	0·2100

Table LIV.—Solubility of Nitrogen in Organic Solvents (Gjaldbaek and Hildebrand)

α = Bunsen Absorption Coefficient. χ_2 = Mole fraction.

Solvent	Temperature, °C.	α	$\chi_2 \times 10^4$
Perfluoroheptane	0	0·411	40·1
	25	0·385	39·1
	50	0·360	38·0
Perfluoromethyl*cyclo*hexane	25	0·375	31·8
Perfluorodimethyl*cyclo*hexane	25	0·317	31·9
	50	0·328	33·0
n-Hexane	25	0·239	14·0
cyclo-Hexane	25	0·156	7·55
Benzene	25	0·124	4·48
Carbon disulphide	25	0·0823	2·23

Table LV.—Solubility of Nitrogen in Organic Polymers

Substance	Temperature, °C.	Pressure, atm.	Solubility (c.c. at N.T.P./c.c., at 1 atm. pressure)	Ref.
Rubber (vulcanized)	25	1	0·035	28
Neoprene (vulcanized)	27·1 36·4 44·1 54·1 65·4 84·7	1	0·054 0·050 0·047 0·044 0·040 0·038	28
Butadiene–acrylonitrile interpolymer	17·0 38·1 48·5 59·5 70·5	1	0·063 0·050 0·048 0·040 0·038	28
Butadiene–methyl methacrylate interpolymer	39·5 55·0 66·0 78·0	1	0·084 0·075 0·071 0·060	28
Butadiene–styrene interpolymer	20·0 35·5 50·0 64·2	1	0·094 0·086 0·082 0·080	28
Polystyrene	170 170	287 118	(c.c. at N.T.P./g.) 7·77 2·95	29

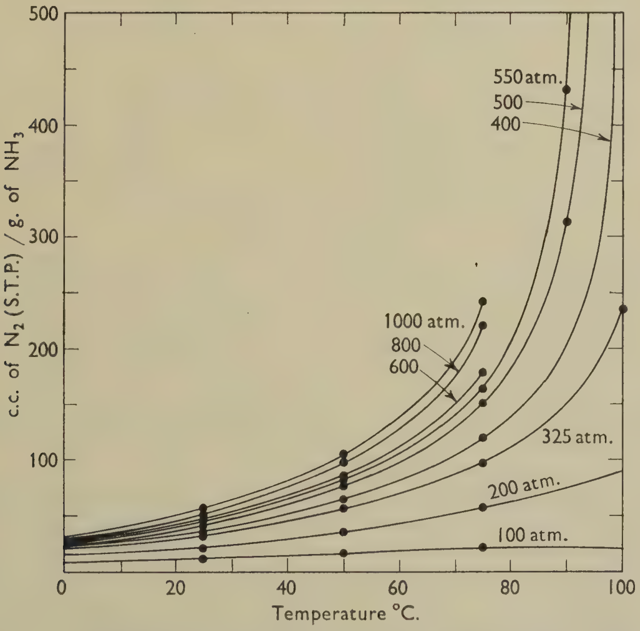

Fig. 23.—Solubility of nitrogen in ammonia, total pressure isobars

Phase Equilibria

NITROGEN–AMMONIA

This is one of the few systems in which phase equilibria have been investigated at very high pressures. Wiebe and Tremearne[37] determined the solubility of nitrogen in liquid ammonia at 25°C. over the pressure range 25 to 1000 atm. This investigation was continued by Wiebe and Gaddy,[38] who determined the solubility at temperatures from 0° to 100°C. and at pressures up to 1000 atm. Their results are given in Fig. 23. Krichevsky and Bolshakov[39, 40] made measurements up to 5600 atm. in the temperature range 90° to 125°C.; Krichevsky and Tsiklis[41–44] extended the pressure range up to 9650 atm. and the temperature range beyond the critical temperature of ammonia ($t_c = +132{\cdot}9$°C.). Isotherms obtained by the Russian school, which show the effect of pressure on the compositions of both phases, are presented in Fig. 24. The critical curve obtained by these workers is given in Fig. 25.

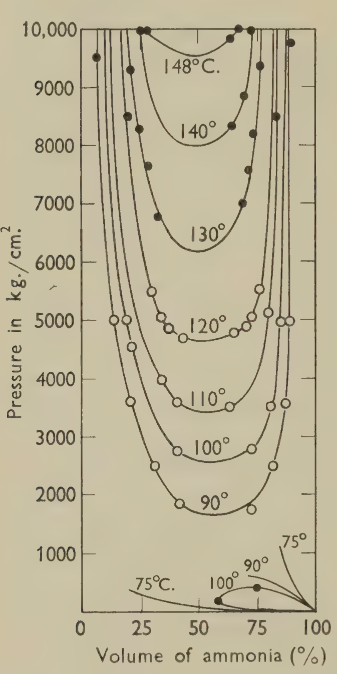

FIG. 24.—Equilibrium of liquid–gas and gas–gas in the ammonia–nitrogen system

● Krichevsky and Tsiklis
○ Krichevsky and Bolshakov

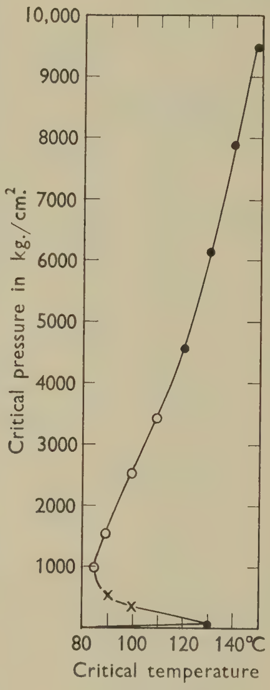

FIG. 25.—Critical curve in the system ammonia–nitrogen

● Krichevsky and Tsiklis
○ Krichevsky and Bolshakov
× Wiebe and Gaddy

They considered that the equilibrium co-existence of two phases at temperatures higher than the critical temperature of the least volatile component (ammonia) must be an example of gas–gas equilibrium.

This type of equilibrium had been predicted earlier from theoretical considerations by van der Waals[45] and by Onnes and Keesom,[46] but until the publication of the Russian work no conclusive experimental evidence had been obtained. Krichevsky and Bolshakov[40] also reported a barotropic phenomenon in which the more dense phase became lighter upon increase of pressure. This type of phenomenon has also been observed in other systems. In order to confirm the results of the Russian workers, Lindroos and Dodge[47] investigated nitrogen–ammonia phase equilibria in the pressure range 1000 to 3750 atm. and in the temperature range 30° to 110°C. As a check on the apparatus, some initial runs were made for comparison with the results of Wiebe and Gaddy. Agreement within ±0·5% was obtained. The isotherms and isobars which were obtained are given in Figs. 26 and 27, respectively. Comparison of Figs. 24 and 26 shows that qualitatively the same type of isotherm is obtained, but quantitatively the results are not in agreement; the reasons for lack of agreement are not clear. One possible factor is that the Russian workers used no means of agitation, but relied merely upon time for the system to equilibrate, only a few minutes being required for the separation of the phases. However, as Lindroos and Dodge point out, diffusion in such dense phases must be slow and for a given phase to become homogeneous would require some considerable time.

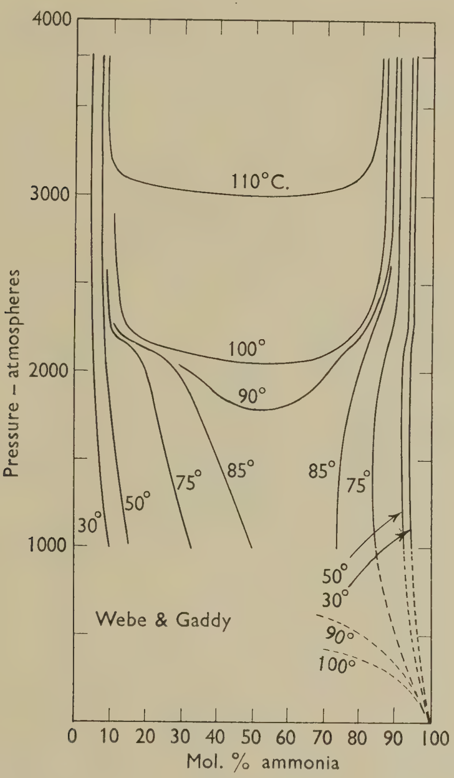

FIG. 26.—Mutual solubility of nitrogen and ammonia.[47] Pressure–composition diagram

Fig. 26 shows that for each isotherm there is a pressure range in which composition is little affected by pressure. For the 30° and 50°C. isotherms, pressure has a negligible effect throughout the entire pressure range; for the 75° and 85°C. isotherms pressures above 2300 atm. have almost no effect on the composition of either phase, whereas below 2300 atm. a decrease in pressure brings the phases closer together in composition. At temperatures above 90°C. pressure has an appreciable effect only near the critical regions. It is interesting to note that the marked changes in the isotherms, especially for the nitrogen-rich phases, occur at about 2000 atm. In this pressure region at about 85–90°C., barotropic phenomena were observed by Krichevsky and Bolshakov. Lindroos and Dodge observed that at all temperatures investigated, and at pressures below 1820 atm., all heavy phases were richer in ammonia, whereas at pressures above 2100 atm., all light phases were richer in ammonia. At some pressure in this range the densities of the phases must be equal. In addition at 90° and 100°C. the phase densities were identical at the critical pressure, 1790 and 2030 atm., respectively. This unfortunate combination of effects, i.e. barotropic phenomena and the critical region, gave rise to considerable experimental difficulty in obtaining true equilibrium samples at 90° and 100°C. The occurrence of the barotropic phenomenon may be explained as follows[47]; at the temperatures and pressures involved, the compressibility of nitrogen is greater than that of ammonia so that the density of the nitrogen-rich phase increases faster than that of the ammonia-rich phase, and exceeds it as the pressure is increased above 1820 to 2100 atm. In the region of the liquid–vapour critical point the difference between liquid and vapour tends to disappear and in fact vanishes completely at the critical point itself. At temperatures and pressures above the critical point it is possible to obtain a gas with a density greater than that of the normal liquid. It is also well known that the transition from liquid to gas and vice versa can occur without any appearance of phase separation.

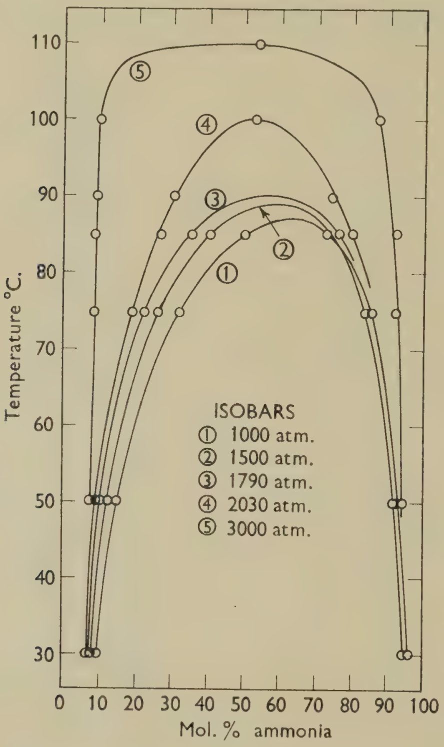

FIG. 27.—Mutual solubility of nitrogen and ammonia.[47] Temperature–composition diagram

Lindroos and Dodge consider, therefore, that in such a compressed gas phase, where the molecules are even closer together than in the liquid phase, it is not surprising that the intermolecular forces would be comparable to those in liquids, and in fact the gases would probably behave like liquids and in some cases exhibit limited mutual solubility. Hence, it is suggested that it would be better to speak of fluid–fluid equilibrium rather than gas–gas equilibrium for such systems. It will be noted from Fig. 26 that below 1000 atm. the Wiebe and Gaddy isotherms show the usual form for ordinary vapour–liquid equilibrium. Fig. 28 shows the critical locus obtained by Wiebe and Gaddy and Lindroos and Dodge.

The Russians, on the basis of their results, expect the complete critical curve to be of the form shown in Fig. 29. The full line represents the Russian experimental data; the dashed line is purely hypothetical, and is drawn merely on the basis that

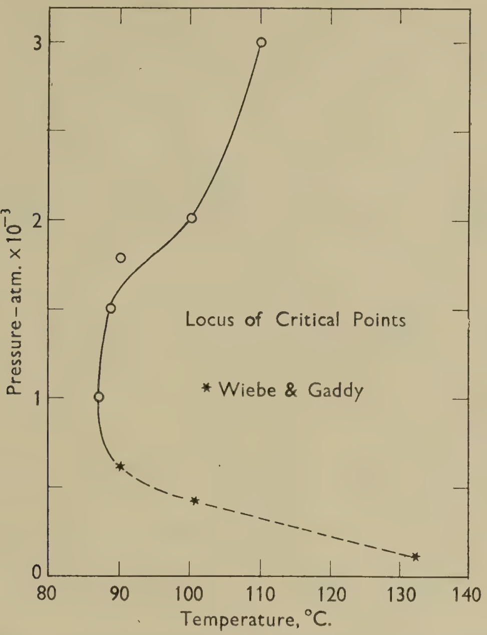

FIG. 28.—Mutual solubility of nitrogen and ammonia.[47] Critical locus curve

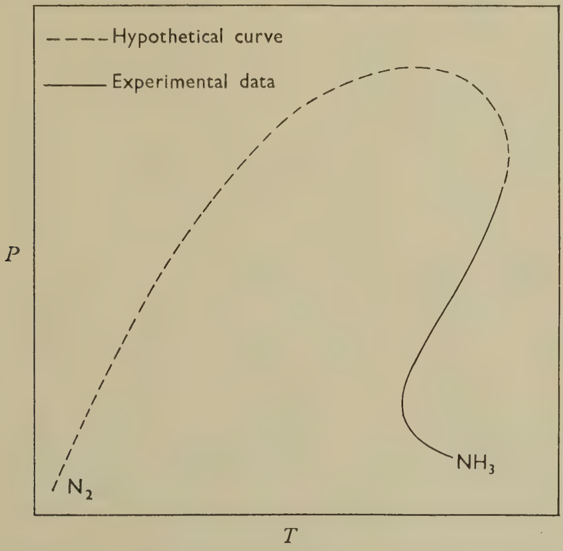

FIG. 29.—Mutual solubility of nitrogen and ammonia.[47] Critical locus curve for the system N_2–NH_3

the critical curve must eventually terminate at the critical point of nitrogen. The assumption that the critical curve is continuous between the two critical points of the pure substances is not necessarily true, especially in view of the fact that ammonia would be an almost non-volatile solid at the critical temperature of nitrogen.[47]

This interesting topic must stimulate further research in the near future and it is hoped that the region of the hypothetical maximum of the critical curve, possibly at about 10,000 atm., will be explored and elucidated.

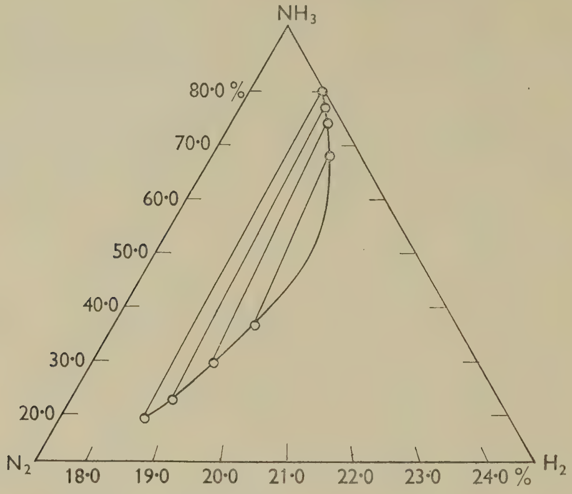

FIG. 30.—Gas–gas equilibrium in the system ammonia–nitrogen–hydrogen[41]

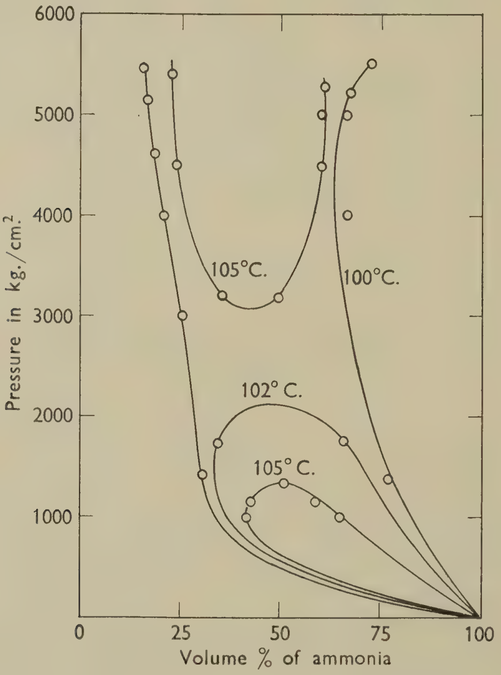

FIG. 31.—Liquid–gas and gas–gas equilibria in the system ammonia–nitrogen–hydrogen.[41] (The ratio between nitrogen and hydrogen in the initial mixture is 1:3)

A nomograph for the solubility of nitrogen in liquid ammonia has been presented by Davis.[48]

NITROGEN–HYDROGEN–AMMONIA

The phase equilibria of this ternary system were investigated by Cupples,[49] Krichevsky and co-workers,[41, 50] and Michels *et al.*[51] The Russian workers report phenomena similar to those in the N_2–NH_3 system (see Figs. 30 and 31).

Michels *et al.* developed a dynamic method for the determination in this system of gas–liquid equilibria which covered the range 10 to 800 atm. and 0° to 120°C. and for mixtures containing 60 to 70% NH_3 observed retrograde condensation when the pressure was lowered.

NITROGEN–METHANE–AMMONIA

The Russian school explored this system also[41, 52, 53] and have observed phenomena similar to those in the nitrogen–hydrogen–ammonia ternary system. Tsiklis[54] reports that the data do not, however, agree with the equation of Krichevsky and Kazarnovski.

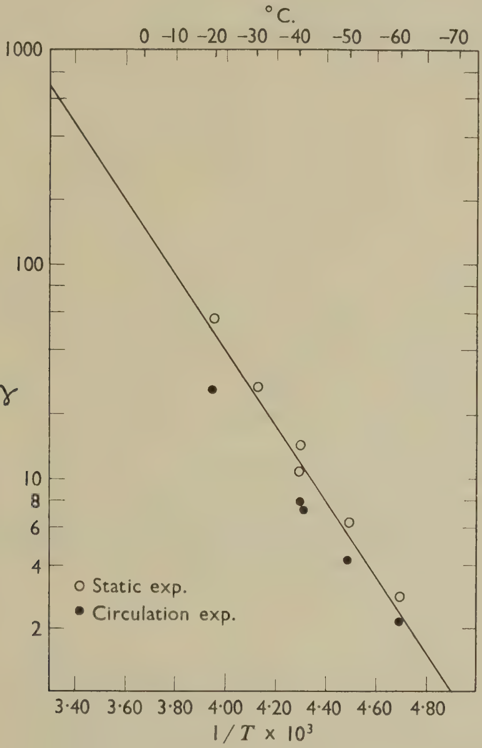

FIG. 32.—Solubility of nitrogen in liquid sulphur dioxide[55]

NITROGEN–LIQUID SULPHUR DIOXODE

Nitrogen is very soluble in liquid sulphur dioxide. From experiments carried out under both static and dynamic conditions, Dornte and Ferguson[55] obtained values for the Kuenen absorption coefficient. Their results are presented in Fig. 32.

> [γ = Vol. of gas in c.c. (N.T.P.) dissolved in 1 g. of liquid at the experimental temperature when the partial pressure of the gas is 1 atm.; T = temperature in °K.]

They found that the system obeyed the equation

$$\log \gamma = 8{\cdot}729 - (8{\cdot}180/4{\cdot}58T)$$

By means of this equation, further solubilities were calculated over the temperature range −20°C. to +30°C. (see Table LVI).

Table LVI.—Calculated Solubility of Nitrogen in Sulphur Dioxide

Temperature, °C.	N_2; c.c.(S.T.P.)/g. SO_2
−20	47
−10	87
0	150
10	260
20	435
30	600

Contrary to expectations this system has a positive temperature coefficient, i.e. the lower the temperature the smaller is the solubility of nitrogen.

Dean and Walls[56] determined the solubility of nitrogen in sulphur dioxide at 83° to −25·7°F. and pressures up to 515 lb./sq. in. These solubilities, given in Fig. 33, are considerably less than those obtained by the previous workers.

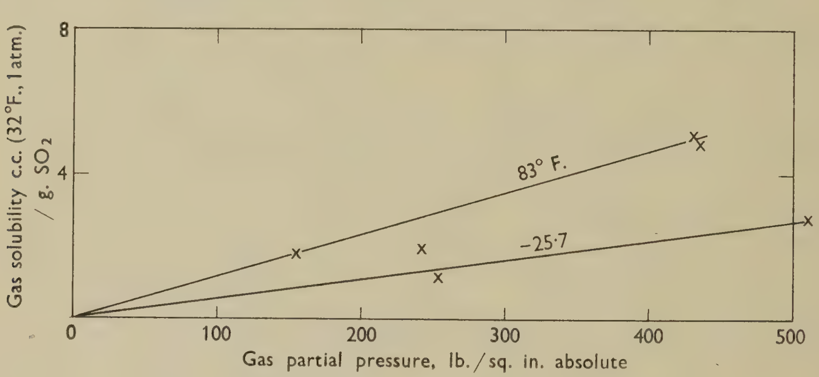

FIG. 33.—Solubility of nitrogen in sulphur dioxide[56]

Tsiklis[57] investigated the sulphur dioxide–nitrogen system at pressures up to 9000 atm. and, as in the nitrogen–ammonia system, the phenomenon of 'gas–gas' equilibria was observed. It is stated that the equation of Krichevsky and Kazarnovsky is valid for this system.

HYDROGEN–LIQUID NITROGEN

The solubility of hydrogen in liquid nitrogen has been reported by several workers.[58–60] The results of Gonikberg, Fastovsky and Gurvich[61] are presented in Fig. 34 as pressure–composition curves at constant temperature.

The solubility of hydrogen in liquid nitrogen obeys the equation

$$N_{H_2} = 1/(A-BT)\%$$

where $\log A = 0{\cdot}469 - 0{\cdot}689 \log (p - p^0{}_{N_2})$,
$\log B = -2{\cdot}1197 - 0{\cdot}444 \log (p - p^0{}_{H_2})$.

The ratio of hydrogen in the gas and liquid phases is given by

$$N'_{H_2}/N_{H_2} = a - b \log (p - p^0{}_{N_2}) + c(p - p^0{}_{N_2})$$

where *a*, *b* and *c* vary with the temperature. Further consideration of the mathematical interpretation of this has been given by the same author.[62, 63]

Fischer[64] developed a graphic method for the determination of the vapour–liquid equilibrium concentrations of a two-component mixture at temperatures and pressures above the critical temperature and the critical pressure of the component having the lower boiling-point. The method is applied to the calculation of the equilibrium isotherms of the nitrogen–hydrogen mixture, the experimental results of Verschoyle being used for the determination of its characteristics.

HELIUM–LIQUID NITROGEN

The solubility of helium in liquid nitrogen at pressures up to 295 atm. and at three different temperatures is given in Table LVII.[65] Investigations by other workers on this system at similar pressures and temperatures have been reported.[66, 67]

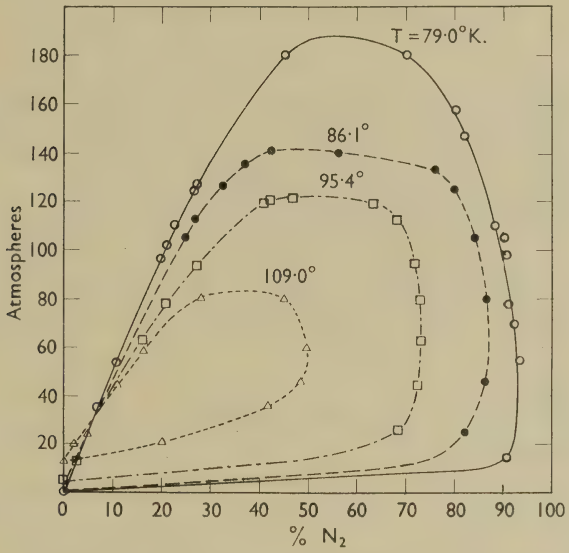

FIG. 34.—Solubility of hydrogen in liquid nitrogen[61]

Table LVII.—Solubility of Helium in Liquid Nitrogen

Temp., °K.	Pressure, kg./sq. cm.	Liquid, % He	Temp., °K.	Pressure, kg./sq. cm.	Liquid, % He	Temp., °K.	Pressure, kg./sq. cm.	Liquid, % He
78	1·1	0·0	90·1	3·5	0·0	109	13·3	0·0
	18·5	0·5		20·7	0·6		27·5	2·3
	44·5	0·9		35·1	1·1		44·5	3·5
	68	1·5		59·0	2·1		81·0	6·2
	105	2·2		95·0	3·5		112·0	8·2
	147	2·6		157	4·9		139·0	10·6
	208	3·7		187	5·6		180	13·1
	269	4·6		220	6·2		232	15·9
	295	5·0		253	7·0		249	16·7
				285	7·9		286	18·3

METHANE–NITROGEN

The methane–nitrogen system is of interest in connection with the removal of nitrogen from some natural gas supplies which may contain more than 10% of nitrogen.

The solubility of solid methane in liquid nitrogen, as reported by Fastovsky and Krestinsky[68] (see Table LVIII) satisfies the relation

$$\log N = 1{\cdot}36576 - 120{\cdot}48/T$$

where N = mole fraction of methane.

Table LVIII.—Solubility of Methane in Liquid Nitrogen

Temperature, °K.	Solubility, % CH_4
70·8	45·15
74·2	54·7
75·2	58·3
77·2	63·7
79·05	69·8

Fedorova[69] has determined the complete solid–liquid phase equilibrium diagram for nitrogen–methane and found it to be of the peritectic type. It has been shown that the solubility of nitrogen in liquid methane at −183°C. is greater than its solubility in liquid propane at the same temperature.[70]

Vapour–liquid equilibrium diagrams for the nitrogen–methane system have been determined by various workers.[71–73] The results of Bloomer and Parent[71] are given in Fig. 35.

Stotler and Benedict[74] successfully fitted an equation of state of the Benedict–Webb–Rubin form to some of the reported data for this system.

ETHANE–NITROGEN

The solubility of ethane in liquid nitrogen expressed as the logarithm of the mole fraction (N_2) is as follows[75]:

°K.	77·3	78·1	78·6
Log N_2	−2·11	−2·09	−2·04

These results are in good agreement with Hildebrand's theory.

ETHYLENE– AND PROPYLENE–LIQUID NITROGEN

The solubilities of ethylene and propylene[76] in liquid nitrogen are given in Table LIX.

Table LIX.—Solubilities of Ethylene and Propylene in Liquid Nitrogen

Ethylene		Propylene	
Temperature, °K.	Solubility, % C_2H_4	Temperature, °K.	Solubility, % C_3H_6
90·1	$1·1 \times 10^{-2}$	83·0	$7·2 \times 10^{-2}$
77·7	$2·24 \times 10^{-3}$	75·0	$7·0 \times 10^{-3}$
69·0	$5·38 \times 10^{-4}$	67·0	$1·7 \times 10^{-3}$

An investigation[77] of the ethylene–nitrogen system at 0°C. and at pressures up to 7000 kg./sq. cm. showed complete miscibility for the two components. The absence of 'limited gas solubility' (cf. nitrogen–ammonia) is attributed to the non-polar nature of the gases.

ACETYLENE–LIQUID NITROGEN AND NITROGEN–OXYGEN

CARBON DIOXIDE–LIQUID NITROGEN AND NITROGEN–OXYGEN

The solubilities of acetylene in liquid nitrogen[78] and liquid oxygen–nitrogen mixtures[79] are given in Table LX. Table LXI gives the solubility of carbon dioxide in the same two solvents.[78, 79]

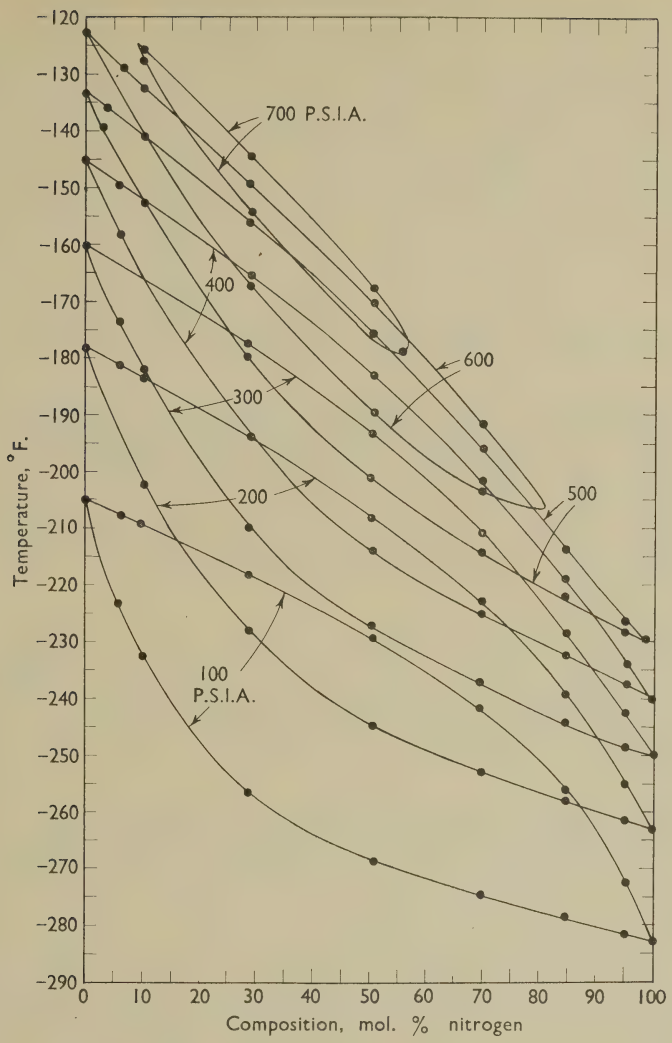

FIG. 35.—Vapour–liquid equilibria; isobaric temperature–composition diagrams, nitrogen–methane system

Table LX.—Solubility of Acetylene in Liquid Nitrogen and Liquid Oxygen–Nitrogen Mixtures

Liquid Nitrogen		Mixtures of Liquid Nitrogen and Oxygen		
Temperature, °K.	Mole fraction C_2H_2 $\times 10^6$	Temperature, °K.	Vol.-% O_2	Mole fraction C_2H_2 $\times 10^6$
95·0	19·95	90·0	99·6	5·9
90·7	13·6	85·6	80·0	5·4
79·4	2·72	82·0	55·0	5·1
68·5	0·955	81·4	50·0	5·0
65·0	0·791	77·4	0·0	4·6

Table LXI.—Solubility of Carbon Dioxide in Liquid Nitrogen and Liquid Nitrogen–Oxygen Mixtures

Liquid Nitrogen		Mixture of Liquid Nitrogen and Oxygen		
Temperature, °K.	Mole fraction CO_2 $\times 10^6$	Temperature, °K.	Vol.-% O_2	Mole fraction CO_2 $\times 10^6$
98	7·26	90·0	99·6	4·5
90	5·34	88·6	80·0	3·7
78·4	3·47	82·0	55·0	—
74·0	—	81·4	50·0	3·0
67·0	2·21	79·4	30·0	2·8
		77·4	0·0	2·5

Phase relationships for the nitrogen–carbon dioxide system are reported.[80–82] Tsiklis[82] states that mixtures of carbon dioxide and nitrogen do not show the effect of ‘partial solubility of gases’ (as with nitrogen–ammonia) at pressures up to 7000 kg./sq. cm., and the equation of Krichevsky and Kazarnovsky was found to fit the experimental data.

The solubility of a $3H_2:1N_2$ mixture in liquid carbon dioxide has been determined at temperatures of 0°, 10° and 20° at pressures up to 203 atm.[83]

BENZENE–NITROGEN

Studies of vapour–liquid equilibria for the benzene–nitrogen system have been reported by various workers.[84–92] Krichevsky and Gamburg[84] investigated the system up to 1100 kg./sq. cm. and over the temperature range 35° to 100°C. Unlike the nitrogen–ammonia system, it affords no evidence of ‘limited mutual gas solubility’. Theoretical interpretations of the nitrogen–benzene system have been discussed.[89, 90]

Krichevsky *et al.*,[91, 92] from their investigations on the system N_2–H_2–benzene at 25°C. and at pressures up to 500 atm., concluded that the simultaneous solubility of nitrogen and hydrogen in benzene satisfied the equation of Krichevsky and Il’inskaya.

PHENANTHRENE–NITROGEN

The solubility of phenanthrene in compressed nitrogen was determined as a function of pressure and temperature by using an absorption-spectra method. For a given nitrogen density the results are consistent with the equation $m = Ae^{-B/T}$, where m is the mass of solute per c.c. of compressed gas and A and B are constants.[93–95] It was noted that the behaviour of saturated solutions of phenanthrene in nitrogen between 0° and 90°C., for densities of nitrogen ranging from 0·3 to 0·6 g./c.c., approximated to that of an ideal solution.

CARBON MONOXIDE–NITROGEN

Vapour–liquid phase equilibria for the nitrogen–carbon monoxide system have been studied.[37, 96–100] Canjar[101] has given an equation of state for carbon monoxide vapour–liquid equilibria. Solid–liquid phase equilibria for the nitrogen–carbon monoxide system show the formation of a complete set of solid solutions.[37, 38, 102]

The vapour–liquid phase relationships of N_2–CO–H_2 mixtures have been determined.[102] Physical data for this system are of importance in connection with the separation of hydrogen from coke-oven gas.

METHANE–HYDROGEN–NITROGEN

The ternary system nitrogen–methane–hydrogen has also been investigated from the vapour–liquid phase equilibria aspect.[60]

METHANOL–NITROGEN

Experimental data on the solubility of methanol in nitrogen for pressures up to 700 atm. and for temperatures from 0° up to 75°C. satisfy the Krichevsky–Khasanova equation.[103] In a theoretical study of this system it was shown that the equation

$$v_s = v_1^0 + BN_2$$

is applicable (where v_s is the molar volume of saturated solution, v_1^0 is the molar volume of pure solute at the pressure of its saturated vapour, and B is an empirical constant).

CARBON TETRACHLORIDE–NITROGEN

The solubility of carbon tetrachloride in compressed nitrogen is given in Table LXII.[88]

Table LXII.—Solubility of Carbon Tetrachloride in Nitrogen
(Solubility expressed as mole fraction × 10^3)

Pressure, atm.	Temperature, °C.				
	−7	0·5	10	25	50
50	—	—	—	4·94	10·3
100	—	—	—	4·59	8·95
200	2·34	3·29	4·44	6·92	12·9
400	6·73	8·42	10·2	14·0	23·0
600	10·8	13·3	15·9	21·6	35·3

ARGON–NITROGEN

The solid–liquid phase diagram for the argon–nitrogen system was reported[48] to show solid solutions with a solubility gap; the possibility of eutectic or peritectic formation was considered. However, more recent work by Din *et al.*[104] shows that a complete series of solid solutions is formed with a temperature minimum below the triple point of nitrogen. Within its limit of accuracy the earlier work agrees with Din's results, but the latter, being more precise, afford the sounder bases for the phase diagram.

Vapour–liquid equilibria for the argon–nitrogen system have been determined by Fastovsky and Petrovsky,[105] but the earlier work of Holst and Hamburger (Mellor, VIII, 59) is considered more reliable.

OXYGEN–NITROGEN

Solid–liquid phase equilibria for the oxygen–nitrogen system have been investigated[106–109]; solid solutions are formed within the range 0–15·7% N_2 and 0–69% O_2 with a eutectic point of 22·5% N_2 at 50·1°K.

The investigation of these equilibria is of importance in the low-temperature separation of air.[109–111] Work at the upper column pressure (ca. 1–3 atm.) (see page 12) has been reported by Cockett[112] whose results are considered to be an improvement on the earlier work of Dodge and Dunbar (Mellor, VIII, 60).

The results calculated by Weishaupt[113] for the binary systems oxygen–nitrogen and argon–nitrogen, from his experiments on the ternary system oxygen–nitrogen–argon at 1000 mm. Hg, are probably less accurate than those obtained by direct experiment.

Results of phase equilibria for the oxygen–nitrogen system below one atmosphere are reported by Armstrong *et al.*[114]; extrapolation of these results shows good agreement with the results of Cockett.

OXYGEN–ARGON–NITROGEN

Liquid–vapour phase equilibria for the ternary system nitrogen–argon–oxygen have been investigated by Weishaupt[113] at a pressure of 1000 mm. of mercury.

The equilibrium curves for this ternary system have been discussed from a theoretical standpoint.[115]

For the solubility of nitrogen in metals the reader is referred to the appropriate metal in the nitride section of this volume.

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ACTIVE NITROGEN

PREPARATION

The following methods of preparation of active nitrogen have been used:

(*a*) continuous discharge[1–5];
(*b*) condensed spark discharge[5–11];
(*c*) direct current impulse discharge[5, 7, 12];
(*d*) electrodeless ring discharge[10, 13–18];
(*e*) arc discharge.[19–21]

The continuous discharge method is the original method of Rayleigh (Mellor, VIII, 83), in which nitrogen at low pressure is subjected to a continuous electrical discharge. The action of the electrical discharge in nitric oxide is also claimed to produce active nitrogen.[22, 23]

Active nitrogen is said to be produced also by the slow thermolysis of aqueous solutions of azides (e.g., sodium and potassium azides, hydrazoic acid).[24–27] Spectral analysis shows this form to be different from 'Rayleigh' active nitrogen.[24, 25] The electrolysis is accompanied by ultra-violet radiation which is independent of the cation; its mean life is $2{\cdot}5 \pm 0{\cdot}2 \times 10^{-3}$ sec. No reaction could be detected[27] between ethylene and nitrogen molecules produced by the thermal decomposition of metallic azides, which indicates that the excited entities in this form of active nitrogen are not the same reactive species as those found in 'Rayleigh' active nitrogen which is known to produce hydrocyanic acid in this particular reaction. No further work appears to have been carried out on 'azide' active nitrogen.

The information given below therefore refers only to the form of active nitrogen obtained by electric discharge in nitrogen.

Effect of Pressure

Kichlu and Basu[28] state that the life of active nitrogen produced by electrodeless discharge increases with decrease in pressure, but Rayleigh[29] doubted the conclusions of these authors. This effect depends on the condition of the discharge vessel; with an 'unclean' surface the afterglow increases in duration and intensity with reduction in pressure, whereas with a 'clean' surface the intensity and duration decrease with pressure.[30] When the discharge tube used for activation is cooled to liquid-air temperature, quenching of the afterglow does not occur at pressures as low as 1 mm.[31]; at this low temperature an afterglow of 15–17 min. duration is observed when the pressure is lowered below 0·1 mm.

Knipp and Scheuermann[15] observed that during the afterglow which follows the electrodeless discharge in nitrogen containing traces of another gas, a flash is seen when the pressure is suddenly increased. The flash has the form of a flat disc which travels onward from the initial point of compression and seems to accompany a pressure pulse. Following the flash the afterglow is still visible and continues to die out gradually. Rayleigh[32] showed that if the volume of the glowing nitrogen is quickly reduced by half, the light emission is reduced by a factor of about 4·3; this is close to the factor 4 which would be expected if the reaction were bimolecular. On compressing the gas by means of a piston the brightness varies as the inverse cube of the volume. Photometric measurements of the luminosity while the gas is being compressed show that the intrinsic brightness varies as the square of the concentration of the active material, indicating a bimolecular reaction in which excess of neutral nitrogen molecules takes no part. This apparently confirms the observation that the time of decay at constant volume between two standard intensities is at low pressures almost independent of the pressure.[33] Other experiments indicate that the effect of pressure on the decay of the afterglow is in agreement with the three-body theory.[34]

Effect of Temperature

Some effects at low temperature have been noted above.[31] It has also been observed that the quenching temperature of the afterglow of active nitrogen increases with increasing pressure, although some theories predict the opposite effect.[31] Willey found that increase of temperature from 20° to 80°C. increases the intensity of afterglow which then gradually decreases[35] from 80°C. to 325°C. In another investigation it was shown that a rise of temperature decreases the intensity and duration of the afterglow in an 'untreated' vessel, whereas in a 'treated' vessel the duration increases and the intensity is slightly enhanced.

Okubo and Hamada[36] observed that pure active nitrogen when heated to about 650°C. glows weakly, but it has the same energy as in the ordinary glowing state. The decay of active nitrogen is bimolecular, but a rise of 100°C. is required to double the rate of decay.[37] Rayleigh[32] established that the brightness of the afterglow varies as $T^{-0\cdot64}$, where T is the absolute temperature.

Wall Effect

Pure nitrogen or nitrogen containing 0·3% of oxygen at about 0·2 mm. Hg exhibits no glow if the vessel is thoroughly baked out and subjected to the action of the electric discharge. Above this pressure a brief glow appears.[30] If water vapour is admitted in amount sufficient to cover the surface of the vessel, the glow is restored to its usual intensity and duration both in pure nitrogen and in nitrogen containing 0·3% of oxygen.[30] It is inferred from these observations that the surface of the vessel governs the visibility of the afterglow in nitrogen.

Rayleigh[38] also showed that preliminary heating of the discharge vessel in vacuo destroys the afterglow, and that heating in nitrogen at 1 atm. pressure has the same effect. Heating in oxygen at even 1 mm. Hg pressure restores the glow.

Herzberg[13] believes that the walls of the vessel have a distinct catalytic effect, producing atomic hydrogen which merely purifies the nitrogen by attacking oxygen. The afterglow of nitrogen, if once removed, can again be obtained by introducing traces of hydrogen; the fluorescence and phosphorescence of quartz and glass are believed to be combined in this phenomenon. Kneser[34] also showed that the walls may exert considerable influence on the afterglow reaction and that the process is usually homogeneous.

Willey[39, 40] has also found that the condition of the container walls (which in turn is dependent on the purity of the nitrogen used) largely determines the mechanism of the decay of the afterglow (proved to be a third order reaction). The impurities (photogens) tend to cover the walls of the discharge vessel. A strong glow appears if the surface of the discharge vessel is covered with paraffin wax and the amount of chemical reaction between the wax and the active nitrogen is much less in photogenic than in non-photogenic nitrogen. These observations show that photogens (e.g. hydrogen) are wall poisons and convert the non-luminous heterogeneous re-association of atoms into a homogeneous reaction accompanied by emission of light.

The catalytic activity of the walls is said to be reduced to a minimum when they are wetted with sulphuric acid or phosphoric acid.[33, 41] Rayleigh[33] showed that with phosphoric acid the glow remains visible for six hours or more and the decomposition reaction is of the second order. Apiezon oil destroys the afterglow, the reaction being apparently of the first order. The maximum prolongation of the life of the afterglow is obtained by coating the wall with a silver film.[42]

The existence of strong wall effects is attributable to adsorption and heterogeneous recombination of nitrogen atoms. Willey[39] concluded that unless the walls of the discharge vessels are 'poisoned' with foreign gases, the recombination process is non-luminous and occurs as a surface reaction. As the concentration of the impurity rises the wall reaction diminishes and the homogeneous decay increases, but above a limit of about 0·1% the impurity reacts chemically with the active nitrogen and interferes with the normal decay. On passing a nitrogen discharge through tubes lined with sodium chloride, lithium chloride or potassium chloride, the surface of the salt is coloured first blue then black.[43] When water vapour is admitted the colour disappears and a solution of the salt gives an alkaline reaction. The colour is also destroyed by heating. The same type of coloration has been observed in a hydrogen discharge tube. When a special attempt is made to eliminate water in the nitrogen discharge, the coloration of the halide is faint and the NH band is barely detectable. The reactions involved may be:

$$\mathrm{N_2}(A^3\Sigma)+\mathrm{H_2O}\rightarrow\mathrm{N_2}(X^1\Sigma)+\mathrm{OH}+\mathrm{H}\quad\text{and}\quad\mathrm{H}+\mathrm{NaCl}\rightarrow\mathrm{HCl}+\mathrm{Na}$$

The OH band at 3064A. is found, but no $\mathrm{HCl^+}$ spectrum.

Effect of Foreign Substances

It is well established now that extremely pure nitrogen does not have an afterglow when first prepared, but the presence of a certain proportion of a foreign gas will produce the afterglow.[44, 39] Bonhoeffer and Kaminsky[44] state that the spectrum of the afterglow is independent of the nature of the impurity. According to Willey these impurities (photogens) 'poison' the walls and prevent recombination of atoms thereupon.[39] In agreement with Rayleigh and with Bonhoeffer and Kaminsky

(Mellor, VIII, 84), Willey found that the optimum concentration of gaseous impurities is about 0·1% and that water vapour is very high in order of effectiveness. No effect of the photogens could be ascribed to their specific natures.

Constantinides[45] found that helium does not affect the afterglow up to pressures ten times that of the nitrogen; other gases shorten the afterglow in the order nitrogen, hydrogen, oxygen. No mention is made in this work however of any precautions to maintain the composition of the nitrogen constant; it is therefore difficult to draw any definite conclusions from it. The negative effect of helium on the afterglow may possibly be explained by the fact[45] that its lowest excitation level (20 v.) is so high that it cannot acquire energy from the active nitrogen and hence has no effect whatever on the glow. It is possible, however, that Constantinides may have used highly photogenic nitrogen and, since the helium could influence neither the state of the walls nor the volume reaction in accordance with the three-body collision theory, the rate of decay would not have been noticeable.[40]

Easily condensible gases (e.g. nitrous oxide, carbon dioxide) reduce wall activity and intensify the glow more than those which are difficult to liquefy (e.g. carbon monoxide, nitrogen); moreover, the retardation of the rate of decay is exactly in the inverse order of the boiling points of the gases concerned (hydrogen b.p. −253°; nitrogen −196°; carbon monoxide −191°; nitrous oxide −90°; carbon dioxide −78°), as was predicted from adsorption theory.[40] With highly photogenic nitrogen (0·12% oxygen) and feeds of carbon monoxide, nitrogen, carbon dioxide and nitrous oxide the decay curves were linear and coincident. The case where the added gas is nitrogen involves a more complicated mechanism in that two factors have to be considered, viz.:

(i) the adsorption or photogen effect; and
(ii) the direct participation by the added nitrogen in the homogeneous glow emission process.

In the electrodeless discharge in mixtures of nitrogen and oxygen at various pressures, a sequence of changes occurs in the character of the afterglow as the pressure is reduced.[27] Within the limits of pressure employed (ca. 1·8 mm. to 0·01 mm. Hg) and from 100 to 60% of oxygen, only the oxygen afterglow, with its maximum afterglow duration, is observed. At lower percentages of oxygen a minimum afterglow duration due to the nitrogen afterglow appears, the latter rising to a maximum duration at a pressure of about 0·035–0·04 mm. Hg. It appears that normal oxygen molecules have marked quenching action on the nitrogen afterglow, but that normal nitrogen molecules have no effect on the oxygen afterglow. Further investigation of the effect of oxygen by Rayleigh[38] showed that when a minute oxygen tributary was added to the nitrogen gas stream, it takes longer to assert its action than the time needed to change the gas composition. This observation indicates that the effect of oxygen is on the walls of the tube, and this is confirmed by the fact that when the oxygen tributary is checked the action persists. The oxygen modifies the glass wall in a way favourable to the accumulation of active nitrogen. The restoration of the afterglow by a tributary oxygen stream is very marked with electrodeless discharges at 0·3 mm., an increase of intensity by a factor of 32 being thus achieved.

Jennings and Linnett[101] consider that these facts indicate that absolutely pure nitrogen will not produce an afterglow because of the rapid removal of nitrogen atoms from the gaseous phase by recombination at the walls, whilst higher concentrations of impurities inhibit the production of the afterglow, since atoms are then removed by chemical reaction.

It is also pointed out that oxygen appears to participate in the glow-emission reaction because of the many levels at which it can absorb energy; therefore its effect should not be considered only on kinetic grounds.

Willey[46] studied the catalytic activity of the metals platinum, iron, silver, zinc, tungsten, molybdenum and copper in accelerating the decay of active nitrogen at various temperatures. In general the ability to cause decay is thought to depend on the stability of the nitride, copper being found to have the greatest activity.

THEORIES OF ACTIVE NITROGEN

Metastable Molecule Theory

The first theory suggested was that of Rayleigh, viz., the atomic nitrogen hypothesis discussed in the original Treatise (Mellor, VIII, 87). From this theory the idea of metastable molecule formation developed. In a later discussion of this subject, Mitra[47] states that if it be assumed that excited nitrogen molecules are formed in the higher vibrational level of the $B^3\Pi g$ state, the emission of the afterglow spectrum (First Positive bands only of the nitrogen molecule) is explained. This reaction is energetically possible if Gaydon's value of 9·76 ev. for the dissociation energy of nitrogen is accepted. The three-body collision,

$$N+N+M \rightarrow N_2(\text{excited})+M(\text{excited})$$

implicit in the metastable molecule theory, would explain the long afterglow. This reaction, however, does not explain why only selected bands of the First Positive group are emitted. To obviate this difficulty Cario and Kaplan[48–50] suggest that active material in the afterglow may consist of metastable molecules in the A state and a mixture of atoms in the ^2P and ^1D states with energies of 3·56 ev. and 2·37 ev. respectively for the atomic states. Furthermore it is supposed that the molecules in the A state are excited to the B state (with the emission of the First Positive band spectrum of the nitrogen molecule) by collision with metastable atoms. Since the energy of the A state is 6·1 ev. the enhancement of the selected bands of the First Positive group can thus be explained. These authors also observed that the metastable molecules appear to be quenched by heating, whereas the metastable atoms are unaffected.

As a result of his researches, Willey[35, 51] reached almost the same conclusion. He found that active nitrogen undergoes a marked decrease in luminosity when led through a second weaker discharge.[35, 42] Its chemical activity, however, as measured by nitrous oxide formation is further increased by this treatment. It is concluded[42] that there are two forms of active nitrogen, viz. the luminous and the chemically active—which are not necessarily co-existent. To explain this it is suggested that active nitrogen consists of a mixture of:

(*a*) metastable diatomic molecules which have a heat of formation of 45,000 g.-cal./g. mol. and are responsible for its chemical activity; and

(*b*) a much smaller proportion (10^{-7}) of atoms which on recombination produce higher energy molecular levels. Their energy (200,000–230,000 g.-cal./g. mol.) is liberated as luminescent radiation as represented by the equation[31]:

$$N+N^*+N_2 = 2N_2+\text{afterglow}$$

where N^* is the 2·3 ev. metastable atom assumed to be chemically active. The left hand side of the equation would account for the third-order decay of the afterglow.

Further support is given to this hypothesis by Tiede and Chomse,[52] who conclude that only the atomic species of active nitrogen can react chemically.

The results of Okubo and Hamada[36, 53] are, however, in complete disagreement with the foregoing conclusions. These workers observed that when a weak discharge is passed through active nitrogen, the loss in energy is coincident with the quenching of the afterglow, and furthermore they did not observe the so-called 'dark modification' of active nitrogen (i.e., the form which is chemically active but has no glow characteristics). Bay and Steiner[9] also reported that a strong afterglow was coincident with a high content of atomic nitrogen.

It is now almost certain that the conclusions of Okubo and Hamada are incorrect. Further research has substantiated the claim that active nitrogen consists largely of molecular species which are chemically active but are not responsible for the afterglow. Rayleigh,[32] for example, observed that when pieces of silver, gold, copper or platinum are exposed to active nitrogen, the metals either melt or become extremely hot and he concluded that the energy of the afterglow is only about 0·001 of the energy collected by the metals. In other words the contribution of the glow process towards the total decay mechanism is small. Herbert *et al.*[54] found no absorption of the nitrogen emission lines corresponding to the metastable atomic states postulated by Cario and Kaplan and therefore conclude that the upper limit of the stationary concentration of the metastable atoms must be of the order of 1/6000%, whereas the Cario–Kaplan theory would require a concentration greater than 1/330%.

Debeau[55] further developed the Cario–Kaplan theory by proposing the following mechanism. Complete dissociation is assumed as the first step, half of the atoms being in the metastable ^2D state and the remainder in the normal ^4S state. A collision complex (NN) is then formed by combination of two atoms; two possible reactions then follow between the collision complex (NN) and a third body M, viz:

$$M+(NN)\begin{array}{l}\nearrow M+N_2(B)\rightarrow N_2(A)+h\nu\ \text{(afterglow)}\\ \searrow M+N_2(^1\Sigma)+\text{heat energy, etc.}\end{array}$$

In support of this mechanism it is known that the afterglow is shown by spectroscopic data to originate in the high vibrational levels in the $B^3\Pi$ state of molecular nitrogen with the production of the metastable $A^3\Sigma$ molecules.

Ionic Theory

Mitra, however,[47] points out that the above theories are mainly concerned with an explanation of the excitation of the characteristic afterglow spectrum and to some extent with its long life; they do not account for its other properties. The so-called 'ionic theory' was proposed[56, 59] to explain the afterglow phenomenon and the chemical activity of active nitrogen. Mitra postulated that a discharge in nitrogen produces N_2^+ ions in the A′ state which drop to the $N_2^+(X')$ state by radiation of the negative bands. Neutralization of the latter ions may occur through collision with the walls of the discharge tube or through three-body collisions with electrons and nitrogen molecules. If the first neutralization process is checked, the three-body process proceeds slowly; this would account for the long duration of the afterglow, the spectrum of which does not show any new bands that can be ascribed to some unknown modification of nitrogen. The production of the afterglow is also facilitated by the presence in the discharge of a gas such as oxygen with a strong electron affinity. The wall effect can be explained by assuming the formation of an adsorbed layer (probably nitrogen), so that only a small fraction of impinging electrons attach themselves to the walls to form an electronic surface charge. The neutralization of N_2^+ ions by surface layer electrons would then not take place, so that recombination would occur in the space as a three-body process, viz.

$$N_2^+ + e + M \rightarrow N_2\ \text{(excited)} + M\ \text{(excited)},$$

during the course of which the afterglow is emitted. It is claimed that this theory is in harmony with the views of Okubo and Hamada, who showed that the maximum energy of excitation which a molecule of active nitrogen can impart to another molecule (or atom) is 9·45 ev., and also with the observation of Rayleigh that active nitrogen delivers to metals at least 10 ev. per molecule of nitrogen. On the other hand experiments carried out with the specific purpose of detecting N_2^+ ions in the glowing gas gave negative results. For instance it was expected that the transition

$$N_2^+(X') + h\nu \rightarrow N_2^+(A')$$

would cause strong absorption in the visible range in the glowing gas. Worley's experiments[60] showed the contrary and indicate that N_2^+ ions are not present in appreciable quantity in the glowing gas, and in agreement with this work, Benson[61] concluded from his experiments that the observed ionization in a stream of active nitrogen is incidental rather than essential to the production of the Rayleigh afterglow and that the ionization appears to be due mainly to electrons. Moreover the concentration of electrons in the glowing gas is many orders less than that of the active particles.

As a result of these criticisms Mitra proposed a new form of the 'atomic theory' which does not require the presence of metastable molecules to explain the afterglow spectrum. This theory is based on the following facts:

1. It is firmly established that the spectrum of the afterglow consists only of selected bands of the First Positive group which originate from the higher vibrational levels $v''=12$, 11, 10 etc. The energy of the highest vibrational level is about 9·7 ev. From this it is inferred that the active substance must be producing nitrogen molecules in the high vibration levels of the B state.
2. The yield of active nitrogen is highest in the neighbourhood of the cathode of the discharge tube. It is also well known that the concentration of positive ions is highest in the neighbourhood of the cathode.
3. Active nitrogen is produced by bombardment of nitrogen by electrons of energy 16·3 ev. which is just above the first ionization potential of nitrogen. The maximum effect begins when the energy is approximately 20 ev., slightly above the second ionization potential of 18·7 ev. This indicates that the bombarding electrons are producing N_2^+ ions in the excited A′ state from which the First Positive bands are emitted.

On this basis Mitra[47] formulated the hypothesis that active nitrogen is a mixture of nitrogen atoms in the metastable states ^2D and ^2P (^2P in small proportion) produced by dissociative recombination of N_2^+ ions with electrons which are always present in a strong electric discharge in nitrogen. The N_2 ions and the electrons are thus considered to be the parents of the active substances rather than being themselves the active substance (as had been proposed in the ionic theory). The process

$$N_2^+ + e \rightarrow \text{N (excited)} + \text{N (excited)}$$

has a high probability and the dissociated atoms may both be in the ^2D state or one in the ^2D and the other in the ^2P state. The energy release on recombination is 15·5 ev. (i.e. the first ionization potential of nitrogen) and the energy required for the production of the excited atoms is the dissociation energy of 9·76 ev. (Gaydon's value) plus the energy of excitation of the two atoms, the latter energy being either 4·74 ev. (for $2 \times {}^2D$ atoms) or 5·93 (for $^2P + {}^2D$ atoms). Hence the total energy for the atomic states could be either 14·50 ev. (i.e. 1·08 ev. less than the ionization potential) or 15·69 (i.e. 0·11 ev. greater than the ionization potential). These differences can, however, be reconciled with theory if the recombining N_2^+ ion is in a low vibrationally excited state or if the colliding electron is sufficiently energetic. Further, ^2D atoms have a long life (8 hours) and do not easily revert to the ground state whereas ^2P atoms have a life of 2·1 sec. and fall to the ground state (^4S) either by radiation or by collision with the wall. In this connection it is interesting to note that Kaplan[62] has observed the line λ3466 due to the transition $^2P \rightarrow {}^4S$. The afterglow arises according to the mechanism proposed by Gaydon, from the recombination of the two ^4S nitrogen atoms colliding on a $^5\Sigma g^+$ potential curve.

The two outstanding properties of active nitrogen (besides its marked chemical activity), namely the prolonged afterglow emitting its characteristic band spectrum and the invariable ionization of the glowing gas, are thus explained. The nitrogen atoms recombine by a pre-association process (as first suggested by Gaydon) to produce nitrogen molecules in the high vibrational levels of the B state from which the First Positive bands with the characteristic intensity distribution are emitted. The long life of the after glow is explained by supposing that the wall recombination of the nitrogen atoms is prevented by the formation of an adsorbed layer of nitrogen molecules on the surface (as was assumed in the ionic theory) and hence the recombination process by the pre-association reaction

$$N(^4S)+N(^4S) \rightarrow N_2\ ^3\Pi g$$

cannot be a fast one.

The marked chemical activity would then be explained by the presence of atomic nitrogen. The constant presence of ions in the glowing gas is explained as resulting from ionizing recombination of metastable atoms:

$$N(^2D)+N(^2P) \rightarrow N_2^+ + e$$

This would explain the fact that although ionization is always associated with the glow process, it is possible to observe ionization even after the glowing gas has been drawn through an 'ion trap'.

The negative temperature coefficient of the afterglow (with increase of temperature the glow intensity falls and with decrease of temperature the intensity increases) can be explained as follows. Pre-dissociation of nitrogen molecules occurs in vibration levels between $v=13$ and 16 of the B state. At higher vibrational levels the predissociation disappears. This means that for the converse process of pre-association the colliding atoms must not possess relative kinetic energies much larger than that with which they were separated at predissociation. It is possible therefore that lowering the temperature brings the kinetic energy of the atoms within this limit and thus increases the chances of pre-association, and that this increased chance more than compensates for the lowering of the rate by the decrease in the number of collisions caused by the lowering of the temperature. Rise of temperature would, of course, have the opposite effect.

The fact that heat destroys the afterglow but not the chemical activity can be explained by the consideration that heating affects only the rate of pre-association of atoms (which produces the afterglow) but cannot affect in any way their chemical activity or their ability to excite the spectrum by three-body collisions. This explanation also accounts for the so-called 'dark modification' of active nitrogen.

The effect of a foreign gas can be interpreted by supposing it to act as a catalytic agent for the formation of the adsorbed layer: the bimolecular decay in the volume observed by Rayleigh would be in agreement with this theory.

A fact unexplained by Mitra's theory is Rayleigh's observation that large amounts of energy are absorbed by metals placed in the active nitrogen stream, though this effect could possibly be due to cathode rays. This experimental result has been confirmed by Cygan,[63] who has offered the following explanations, though these are considered by Rayleigh to be unimportant:

(i) existence of condenser field;
(ii) electron activation of nitrogen in the vicinity of the foil;
(iii) energy transfer to foil by electrons.

According to calculations Rayleigh's energy measurement could be provided by electrons but not by ions. Another factor unexplained by Mitra's theory is the discrepancy between the observed spectrum and that deduced by theory. Further evidence against Mitra's theory was provided by Benson (see page 125).

Oldenberg[64] has suggested that the primary particles are nitrogen atoms, which by three-body collisions give metastable molecules of nitrogen in the $A^3\Sigma_u^+$ state and metastable nitrogen atoms in the ^2P and ^2D states. The afterglow occurs by transfer of the excitation energy from the metastable atoms to the A state molecules which are thus raised to the B $^3\Pi g$ state. However, Stanley[21] points out a defect similar to that found in Mitra's theory, viz., that there can be no change with pressure of the relative vibrational entry rate into the nitrogen (B) state provided that the temperature is held constant.

A modification of Mitra's theory has been discussed by Stanley whereby the afterglow reaction should be represented by a three-body collision process, e.g.

$$N(^4S)+N(^4S)+N_2(v_1) \rightarrow N_2(B^3\Pi g)+N_2(v_2)$$

v_1 and v_2 denoting the initial and final velocities of the inert third body.

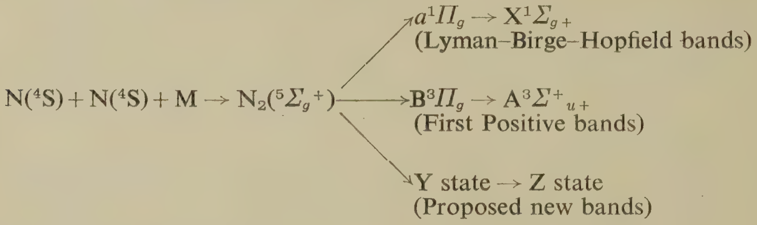
(Cf. Mitra's reaction $N(^4S)+N(^4S) \rightarrow N_2(B^3\Pi g)$)

Stanley's observation would also be in accordance with Rayleigh's observations that the glow intensity varies:

(i) as the cube of the concentration when the volume of the activated gas as a whole is changed;
(ii) as the square of the concentration of the active particles when the inert gas pressure is held constant; and
(iii) directly as the pressure when the concentration of active particles is held constant.

Pre-association Theory

A review covering some of these data up to 1945 has been presented by Mitra,[65] and this is supplemented by another review (1958) by Jennings and Linnett.[101] The latter authors have put forward a pre-association theory for the afterglow system which is represented schematically as follows:



$$N(^4S)+N(^4S)+M \rightarrow N_2(^5\Sigma_g{}^+) \begin{array}{l} \nearrow a^1\Pi_g \rightarrow X^1\Sigma_{g+} \ \text{(Lyman–Birge–Hopfield bands)} \\ \rightarrow B^3\Pi_g \rightarrow A^3\Sigma^+{}_{u+} \ \text{(First Positive bands)} \\ \searrow \text{Y state} \rightarrow \text{Z state} \ \text{(Proposed new bands)} \end{array}$$

Jennings and Linnett claim that:

(i) Charged particles play no part in the production of the afterglow.
(ii) The only species present in active nitrogen in appreciable concentration are atoms and molecules in the ground state; the former are responsible for the chemical reactivity.
(iii) The pre-association theory succeeds in explaining the experimental observations and is able to account for the different band systems in the afterglow.

PHYSICAL PROPERTIES OF ACTIVE NITROGEN

Spectra

Some aspects of the spectra of active nitrogen have been discussed in the section on 'theories of active nitrogen'.

A mass spectral investigation has been carried out[41] by passing purified nitrogen through a discharge tube at pressures of 0·64 to 2·24 mm. Hg at a flow rate of $1{\cdot}03 \times 10^{-5}$ moles/sec., the walls of the discharge tube and the glass tubing leading to the spectrometer being 'poisoned' with metaphosphoric acid. When the discharge tube was excited the ion intensity corresponding to mass 28 decreased, while that for mass 14 increased, suggesting the presence of atomic nitrogen. No peaks other than 28 and 14 were observed. Measurements of the ion intensities as a function of electron energy with and without the discharge again suggested the presence of atomic nitrogen in the discharge.

Kaplan and Rubens[66] have confirmed the earlier observation of the presence of the auroral green line $\lambda 5577$; this is accompanied by the forbidden lines of oxygen $\lambda 2972$ and of nitrogen $\lambda 3467$ and the Vegard–Kaplan bands, showing that the emission of forbidden radiations is a primary radiative process in these afterglows.

Stanley[21] reports that the afterglow spectrum at low pressures contains the α bands of the nitrogen First Positive system, the β and γ bands of nitrous oxide, the OH (0, 0) and (1, 0) bands, the NH (0, 0) and (1, 1) bands, and at higher pressures some of the CN violet system. As the pressure increases from a few mm. of mercury the other bands of the nitrogen First Positive system appear in addition to the α bands and their intensity relative to that of the α band continues to increase until, at pressures approaching 1 atm., the markedly anomalous intensity distribution so characteristic of the low-pressure glow has given way to much more uniform distribution somewhat similar to that of an ordinary positive column low-pressure discharge spectrum. Jennings and Linnett[101] state that from spectral evidence the only species present in active nitrogen in appreciable concentrations are atoms and molecules in the ground state.

Effect of Magnetic Field

The Stern–Gerlach experiment has been applied to a study of a beam of active nitrogen. No deflection of the beam was obtained,[61, 67–69] and it was concluded that the concentration of N_2^+ ions is small. According to Kane and Clark[70] the effect of a magnetic field is to decrease the decay rate, owing to impeded diffusion of the ions to the walls.

Ionization and Conductivity

Constantinides[45] attributed the conductivity of active nitrogen to electrons emitted from the surface of the electrodes either photo-electrically or by direct action of the active nitrogen on the metal. This result was confirmed by Willey and Stringfellow.[6, 71] The production of active nitrogen increases suddenly when the accelerating potential of the electrons attains 16·0 v. which is approximately the first ionization potential of nitrogen.[72] Above this potential the production increases gradually. It is also reported that electrons having energies exceeding 20 ev. are present in the afterglow.[73] Rayleigh[38] has shown that the ionization associated with afterglowing nitrogen is completely cut off if the test vessel is separated from the afterglow by a silica wall: hence the ionization is not produced by light (at least of wave-length greater than 1850 A). No increased current was observed when the surface action was such as to make a testing cathode red hot, and this seems to exclude electron emission as the cause of ionization. Rayleigh further showed that the ionization process and the afterglow process are in some measure independent. Some of the recent observations of Benson[61, 67] on ionization are discussed under theories of active nitrogen. Microwave measurements by this author showed that the free electron density was of the order of 1 free electron for each $2{\cdot}3 \times 10^8$ molecules, which appears to be high enough to account for the glow discharges in the stream at regions of low pressure. Probes in the active nitrogen stream responded to negative sign particles only.

Other physical measurements made by Benson show that the viscosity is the same as that of ordinary nitrogen and, by calorimetric experiments, that the decay of the afterglow occurred with the evolution of energy equivalent to 22·3 g.-cal. per g. of gas, which corresponds to an excitation of one in 350 of the molecules present to an energy of 9·6 ev.

CHEMISTRY OF ACTIVE NITROGEN

Active nitrogen and atomic hydrogen react to form ammonia.[2, 52, 74–77] The amount of ammonia formed is proportional to the concentration of hydrogen atoms so long as the nitrogen atoms are present in excess.[77] By means of an apparatus[75] in which it was possible to activate nitrogen and hydrogen by electric discharge separately before reaction occurred, Steiner observed the following phenomena: hydrogen atoms show no reaction with nitrogen molecules; the reaction between nitrogen atoms and hydrogen atoms gives ammonia, while the reaction between nitrogen atoms and hydrogen molecules produces hydrazine and ammonia, the former in much the smaller quantity. Probably ammonia is formed through a triple collision:

$$N + H + X \rightarrow NH + X'$$

followed by the reaction of NH with molecular hydrogen:

$$NH + H_2 \rightarrow NH_3$$

while the hydrazine arises thus:

$$N + H_2 + X \rightarrow NH_2 + X'' \quad \text{and} \quad 2NH_2 \rightarrow N_2H_4$$

The formation of ammonia is greatly accelerated by an iron, nickel or copper surface, whereas the rate of formation of hydrazine is considerably reduced.[79] The ability of electrode metals to adsorb nitrogen atoms and thereby accelerate their union to molecules increases in the order: aluminium, tungsten, nickel, iron, copper and platinum[2]; the yield of ammonia increases in the order: tungsten, aluminium, nickel, copper, iron, platinum.

Mixing nitrogen and hydrogen, separately activated, and then mixing with carbon monoxide at 115° results in the formation of urea.[80]

The supposedly oxidizable variety of active nitrogen has received further attention.[79, 81] No evidence was found for any oxidizable modification or for any oxide of nitrogen which reacts with ozone but not with oxygen.

Pure dry nitrogen activated by a 20,000 v. discharge lowers the temperature at which a carbon monoxide–air mixture ignites spontaneously.[82] Active nitrogen catalyses the transformation of carbon monoxide into carbon dioxide and carbon.[81, 83]

The spectrum of iodine excited by active nitrogen shows a line at 185 mμ and also the iodine line at 206 mμ. When the pressure of iodine vapour is comparable with that of the active nitrogen the visible reaction is an instantaneous flash. It is unlikely that there is any chemical reaction; the iodine probably receives energy and radiates it again.[84]

The catalytic activity of active carbon is reduced when it is prepared from lactose and subsequently treated with active nitrogen and nitric oxide.[85]

When nitrogen and hydrogen bromide at low pressures are passed through an electrodeless discharge, ammonium bromide and bromine are formed and a yellow-to-orange afterglow is observed if traces of water vapour are present, but the afterglow is absent if the nitrogen is dry and free from oxygen or oxygen compounds. With hydrogen iodide an intense brilliant blue glow is obtained, but with hydrogen chloride no afterglow is observed.[86]

When an arc is burned between iron poles in an atmosphere of nitrogen, the nitride Fe_4N_2 is formed.[19] Examination of the arc with a spectrometer failed to reveal the bands characteristic of the nitrogen afterglow spectrum. This result was interpreted as showing either that the active nitrogen is non-luminous or that under the more intense current of the arc, as compared with the condenser discharge, another chemically more active modification of nitrogen is produced.

In an investigation of the film adsorbed on tungsten from active nitrogen, Langmuir concluded that this was not nitrogen but oxygen, presumably from oxygen present as an impurity in the nitrogen.[87]

The reaction of active nitrogen with mercury[52, 88, 89] is to cause excitation of the metal with the emission of the resonance spectrum of the metal at 2537 A. Under similar experimental conditions the resonance spectra of zinc and cadmium are not observed.

The action of active nitrogen on hydrocarbons has been investigated by Winkler using methane, ethane, propane, propylene, ethylene, acetylene and various butenes. The main product of the reactions is hydrocyanic acid; small quantities of polymerized hydrocarbons and breakdown products are also formed.[90–96] Hydrocyanic acid and other breakdown products are also formed in the reaction between active nitrogen and diphenylacetylene.[1]

ACTIVATED NITROGEN MOLECULES AND ATOMS FORMED AT LOW TEMPERATURES

If nitrogen gas at 0·1–3 mm. Hg pressure is passed through an electrodeless discharge and then frozen at about 4·2°K., the solid nitrogen emits a green or blue glow with intermittent brilliant blue flashes. This emission is connected with the presence of free nitrogen atoms in the solid lattice.[57] It has been further established that the blue-green afterglow occurs when the solid reaches a temperature of 28–35°K.[98, 99] Temperatures and spectral measurements give further indications of the presence of atomic nitrogen in the solid to the extent of about 0·2%.[78, 100]

Similar discharges through hydrogen, oxygen and water vapour and subsequent freezing of the vapour with liquid helium have produced solid deposits in which atoms of hydrogen and oxygen and the free radical OH have been detected.[97]

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VALENCE

MODERN CONCEPT

The concept of valency has changed considerably over the past few decades with the development of wave mechanics and its application to chemistry, in particular to the structures and the geometry of molecules (see Pauling,[1] Pauling and Wilson,[2] Coulson,[3] Mills[4]). The earlier historical development of valency as applied to nitrogen has already been given (Mellor, VIII, 89). A brief account of the modern concept of the valency of nitrogen is given below (see Coulson[3], Orville Thomas[5] and Cartmell and Fowles[6]).

The very close similarity in electronic structure of carbon and nitrogen leads to considerable similarity in the electron distribution and the geometry of their corresponding compounds. Indeed for some purposes one might usefully regard a given nitrogen compound as being 'derived' from the corresponding carbon compound by adding a positive charge to the carbon nucleus; for example CH_4 and NH_4^+ are similar in electron distribution and geometry. Other obvious similarities appear in the discussion below.

In the nitrogen atom there are seven extranuclear electrons, two in the 1st quantum group and five in the 2nd, thus:

$$1s^2 \quad 2s^2 \quad 2px^1 \quad 2py^1 \quad 2pz^1$$
$$\text{(Compare carbon} \quad 1s^2 \quad 2s^1 \quad 2px^1 \quad 2py^1)$$

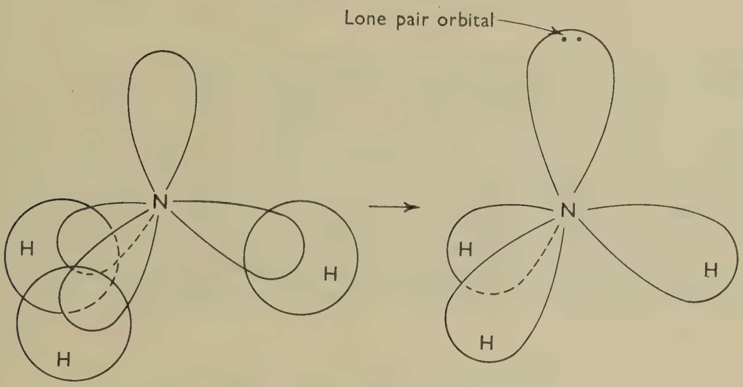


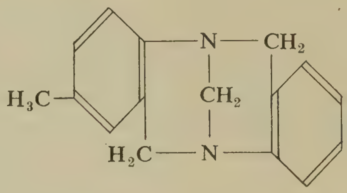
FIG. 36.—The ammonia molecule

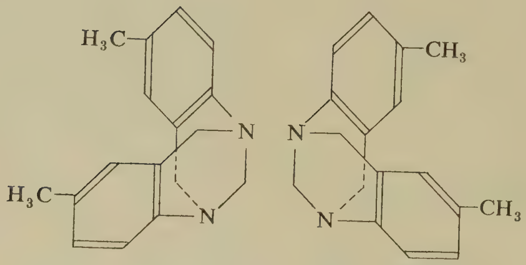
In compounds of the type NR_3, where single bonds are involved, the five valence electrons in the 2nd quantum group are essentially tetrahedrally hybridized giving a tetrahedral model with a lone pair of electrons at the 4th apex. The ammonia molecule is represented as in Fig. 36.

Actually the four orbitals are not identical in this case (compare C in CH_4 where they are identical), the three orbitals bonding with the hydrogen nuclei being slightly different from the orbital which accommodates the lone pair; the orbitals are designated by Orville-Thomas[5] thus:

$$3(2p+\delta 2s)+1(2s+\delta 2p)$$

This geometry in a compound $R_1R_2R_3N$ would lead one to expect optical activity, but this has never been observed (cf. Mellor, VIII, 90). This is probably because of the high rate of inversion of such compounds, i.e. the net passage of the nitrogen through the plane of the other three groups, the so-called 'umbrella effect', which is known to occur in the case of ammonia. One amine, actually a diamine, has been resolved but this is a special case involving a cage-like structure, viz., Trögers base[7] formulated thus:





PENTAVALENT NITROGEN

So-called pentavalent nitrogen (i.e., 4 co-valent nitrogen) is exhibited in ammonium compounds (e.g. $NH_4^+ X^-$), substituted ammonium compounds of the type $(NR_4)^+ X^-$ and amine oxides (R_3NO). In these compounds the four groups attached by covalent links to the central nitrogen atom are oriented tetrahedrally. Suitable examples of the quaternary ammonium salts and the amine oxides have been resolved into their enantiomorphs by classical methods (see Mills and Warren for example, Mellor, VIII, 91). However, ammonium salts of the type $(NHR_1R_2R_3)^+ X^-$ have not been resolved and this is presumably due to the ease of transfer of a proton from the nitrogen to an acceptor, e.g., the anion or the solvent molecule, giving the amine which is capable of inversion (vide supra, 'umbrella effect').[8]

MULTIPLE BONDED NITROGEN

Compounds of nitrogen involving multiple bonded nitrogen are comparable with the carbon compounds the ethylenes and acetylenes.

Where nitrogen is involved in double bonds, for example in azo compounds containing —N=N—, the nitrogen is best regarded as trigonally hybridized, having three coplanar hybrid sp^2 orbitals mutually oriented at 120° and an atomic p orbital perpendicular to the plane.

In the formation of double bonds overlap of sp^2 hybrid orbitals takes place with the formation of a σ bond and lateral overlap of the two atomic p orbitals gives rise to a π bond with a planar distribution of groups about the double bond (cf. ethylenes), as shown in Fig. 37.

The double bond restricts rotation and gives rise to the possibility of *cis-trans* isomerism; for example *cis-* and *trans*-azobenzenes have been isolated by Cook.[9] In the oximes, semi-carbazides and hydrazones the double bond may be similarly formulated. This also gives rise to *cis-trans* isomerism in suitable cases (cf. Mellor, VIII, 92), as shown in Fig. 38.

In aromatic structures, e.g. pyridine, quinoline, *iso*quinoline, pyrimidines, etc., nitrogen is similarly hybridized and interacts with similarly hybridized carbon atoms giving rise to aromatic systems closely resembling benzenoid structures (see Coulson[3] and Dewar[10]). In 5-membered heterocyclics, e.g. pyrrole, pyrazole, similarly trigonally hybridized nitrogen atoms are involved.

In triply bonded nitrogen compounds, e.g. cyanides, diazonium compounds, etc., the nitrogen is digonally hybridized, there being two collinear *sp* hybrid orbitals and two atomic *p* orbitals at right angles to these. The *sp* hybrids can overlap with suitable orbitals of other atoms giving rise to σ bonds and the *p* orbitals overlap laterally with other *p* orbitals giving 2π bonds, as in Fig. 39.

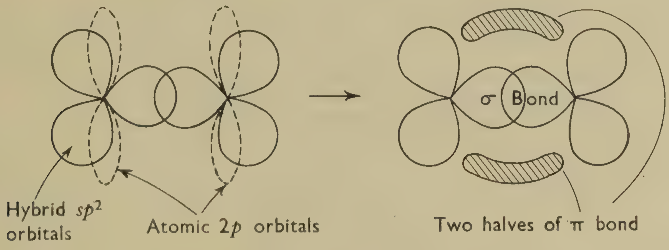


FIG. 37.—Double bonded nitrogen atoms

This 2π bond system actually constitutes an electron system having cylindrical symmetry, as in acetylene, etc. (cf. Coulson[3]).

The electronic structure of molecular nitrogen is best described by the molecular orbital method (cf. Coulson[3]).

$$\begin{aligned}&N(1s^2 \quad 2s^2 \quad 2p^3)+N(1s^2 \quad 2s^2 \quad 2p^3)\\ \rightarrow\ &N_2(KK \quad (z\sigma)^2 \quad (y\sigma)^2 \quad (x\sigma)^2 \quad (w\pi)^4)\end{aligned}$$

KK denotes that the two *K* shells of the atoms are filled by non-valence electrons.

The classical designation of the triple bonding of nitrogen by $N \equiv N$ (six electrons being involved) is given in the molecular orbital notation above by $(x\sigma)^2$ $(w\pi)^4$, i.e. one σ bond and two π bonds at right angles to each other. Thus the extraordinary stability of the nitrogen molecule relative to oxygen and fluorine can be directly attributed to the fact that the nitrogen molecule has just enough electrons to fill the bonding π orbitals, whereas in oxygen and fluorine the extra-nuclear electrons occupy antibonding π orbitals.

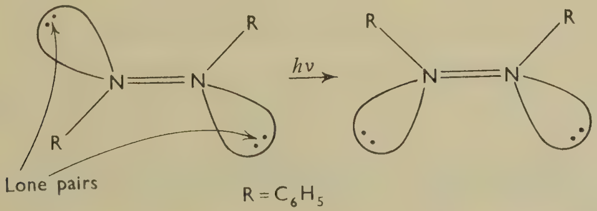


FIG. 38.—*cis-trans* isomerism in nitrogen compounds

CHEMISTRY OF NITROGEN

The chemistry of nitrogen is dealt with in the section of this volume dealing with the nitrides of the metals and under the accounts of non-metals which will be found in other volumes.

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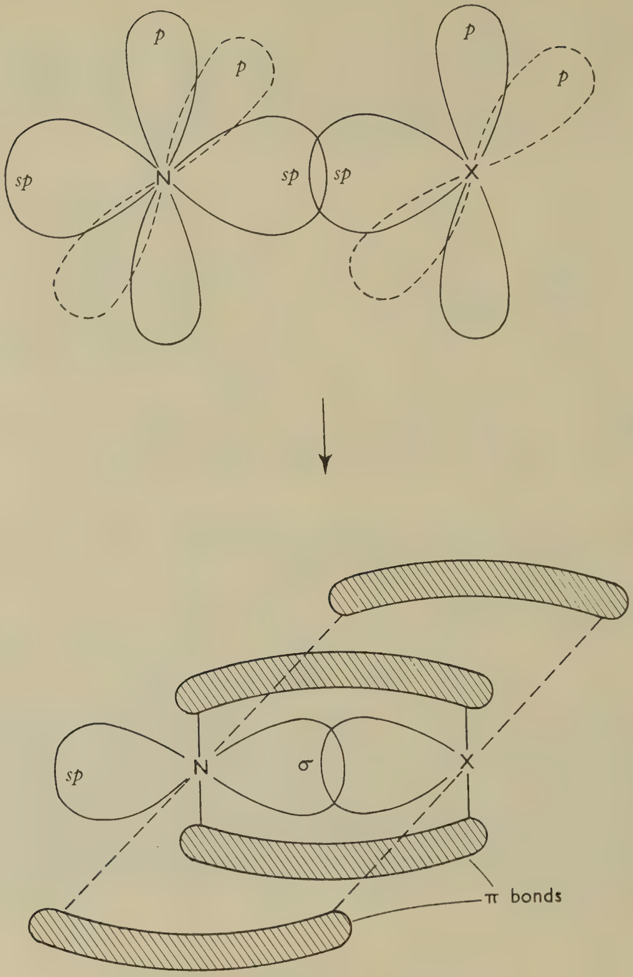

FIG. 39.—2π bonding of nitrogen atoms

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ATOMIC WEIGHT AND ISOTOPES OF NITROGEN

ATOMIC WEIGHT

The determinations of the atomic weight of nitrogen made in the period surveyed in this Supplement are given in Table LXIII, the values being expressed on the usual chemical scale.

Table LXIII.—Atomic Weight of Nitrogen

Authors	Year	Basis	Result	Ref.
Moles	1927	N_2 limiting density based on average values of constants of other authors	14·0082 ± 0·0002	1
Moles & Clavera	1927	N_2 limiting density	14·0082 ± 0·00042	
Moles	1929	Review	14·008	2
Moles & Batuecas	1930	NH_3 limiting density	14·009	3
Baxter & Greene	1931	Chemical analysis Ratio Ag : NH_3 ($NH_3 \rightarrow NH_4Cl \rightarrow AgCl$)	14·0078	4
Batuecas	1931	N_2O limiting density	14·007	5
Moles	1932	Corrected results of preceding data	14·008	6
Cawood & Patterson	1933	N_2O limiting density	14·008	7
Dietrichson, Orleman & Rubin	1933	NH_3 limiting density	14·0066	8
Moles & Sancho	1934	NH_3 limiting density	14·008 ± 0·001	9
Moles & Salazar	1934	N_2 limiting density	14·0083	10
Cawood	1935	N_2O limiting ratio with oxygen	14·006	11
Hönigschmid & Schlee	1936	Chemical analysis ($AgNO_3 \rightarrow AgCl$)	14·009 ± 0·003	12
Moles & Toral	1936	N_2O limiting density	14·008	13
Moles & Sancho	1936	NH_3 limiting density	14·009 ± 0·001	14
Cawood & Patterson	1936	N_2O limiting density	14·007	15
Moles	1937	N_2 limiting density	14·0083	
		N_2O ,, ,,	14·0083	
		NH_3 ,, ,,	14·0079	16
Moles & Toral	1938	N_2O limiting density	14·0083 ± 0·0005	17
Hönigschmid & Johanssen-Gröhling	1946	$NH_4Cl:Ag:AgCl$ $NH_4Br:Ag:AgBr$	14·008 ± 0·0004	18
Lambert & Phillips	1950	Microbalance: limiting ratio N/O and CH_4/N	14·0078	19
Moles	1950	N_2 limiting density	14·0085	20
Batuecas & Casado	1952	N_2O limiting density	14·009 ± 0·001	21

Bainbridge[22] calculated from his mass spectrograph results that the chemical atomic weight of nitrogen is 14·00730 ± 0·00002; this is based on an abundance ratio ($^{14}N/^{15}N$) of 273:1 using the conversion factor of 1·0002783 ± 0·0000005 for the physical and chemical atomic weight scales.

As a result of the possible variation in the relative abundance of the nitrogen isotopes from different sources, the maximum variation in the atomic weight as calculated by Urey[23] is 0·00016, which would be insignificant for all chemical work.

The value accepted by the International Commission on Atomic Weights (1953) is 14·008.[24]

NITROGEN ISOTOPES

Six isotopes of nitrogen are known; two of these, ^{14}N and ^{15}N, are stable isotopes which occur naturally; the other four isotopes ^{12}N, ^{13}N, ^{16}N, ^{17}N are radioactive, and have been prepared artificially by nuclear reactions.

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Stable Isotopes

Aston[25] assumed from his mass spectrograph results that nitrogen was a simple element, as was expected from its chemical atomic weight of 14·008. With the discovery of the isotopic nature of oxygen and the resultant shift of the mass scale a search was made for heavier isotopes of nitrogen. ^{15}N was discovered by Naudé[26] in the band spectra of NO. Support for Naudé's work was given by Herzberg.[27] Table LXIV gives the abundance ratio and atomic masses of ^{14}N and ^{15}N (on the scale $^{16}O = 16·0000$) as determined by physical methods.

Table LXIV.—Abundance Ratio and Atomic Masses of the Isotopes of Nitrogen Determined by Physical Methods

Authors	Year	Ref.	Atomic Masses $^{16}O = 16$		Abundance Ratio $^{14}N/^{15}N$
			^{14}N	^{15}N	
Naudé	1929	26			700 ± 140
Herzberg	1930	27			800/1
Birge & Menzel	1931	28			320/1
Urey & Murphy	1931	29			347/1
Urey & Murphy	1932	30			346/1
Vaughan, Williams & Tate	1934	31			265/1
Wahl, Huffman & Hipple	1935	32			265/1
Lawrence, McMillan & Henderson	1935	33	14·0069		
Aston	1936	34	14·0073 ±0·0005		
Bainbridge & Jordan	1936	35	14·0076		
Bainbridge & Jordan	1936	36		15·0050 ±0·0003	
Mattauch	1938	37	14·00756		
Asada, Okuda, Ogata & Yosimoto	1939	38	14·00761		
Asada, Okuda, Ogata & Yosimoto	1940	39	14·00761		
Ewald	1946	40		15·004934	
Cohen & Hornyak	1947	41	14·007539 ±0·000015		
Bainbridge	1948	42	14·00754		
Tollestrup, Fowler & Lauritsen	1950	43	14·00751[(a)] 14·007565[(b)]		
Nier	1950	44			273/1 {99·635% ^{14}N 0·365% ^{15}N
Roberts	1951	45	14·007544		
Ewald	1951	46	14·007525	15·004928	
Dzhelepov & Zyryanova	1952	47	14·007531	15·004877	
Ogata & Matsuda	1953	48	14·007550	15·004902 ±0·000009	
Ogata & Matsuda	1953	49	14·007551	15·004905 ±0·000006	

(*a*) From nuclear *Q* values. (*b*) From spectroscopic data.

The abundance ratio $^{14}N/^{15}N$ of 273/1 obtained by Nier[44] is the value generally accepted.

The 'packing fractions' of the nitrogen isotopes, i.e. the values of the quantity (atomic mass—mass number) × 10^4/mass number, are 5·4 and 3·3 for ^{14}N and ^{15}N respectively.[50]

Abundance Ratio of Nitrogen from Different Sources

Cady and Beecher[51] compared the atomic weights of nitrogen in a sample of gas trapped in fergusonite and a sample of nitrogen obtained from ammonium chloride; they concluded that there was no significant difference in the atomic weight. The isotopic ratio of nitrogen occluded in radioactive materials was investigated by White and Yagoda.[52] It would appear from their results (see Table LXV) that the ^{15}N content of a radioactive material is directly proportional to the age of the specimen.

Several hypotheses have been advanced in explanation of this time dependent proportionality. White and Yagoda themselves suggest that the more rapid diffusion of the lighter nuclide ^{14}N would increase the percentage abundance of ^{15}N, and that the greater the time of diffusion, the greater would be the increase.

Table LXV.—Isotopic Constitution of Nitrogen in Radioactive Minerals

Sources of Nitrogen	Partial Composition		Age 10^6 yrs.	$^{15}N\%$	$^{14}N/^{15}N$
	$U_3O_8\%$	$ThO_2\%$			
Pitchblende, Woodsmine, Central City, Colo., U.S.A.	76·7	0·018	57	0·532	187
Pitchblende, Vein 2, Great Bear Lake, Canada	63·6	not given	1251	0·586	170
Pitchblende, Katanga, Belgian Congo	78·8	not given	625	0·575	173
Pitchblende, Shinkolobwe, Katanga	~89	not given	625	0·574	173
Uraninite, Wilberforce, Canada	72·5	10·6	1050	0·614	162
Uraninite, Sprucepine, N.C., U.S.A.	~91	3	251	0·546	182
Samarskite, Sprucepine	11·3	0·8	250	0·549	181
Monazite sand, India	trace	(Th 10)	unknown	0·600	166
Atmospheric nitrogen } Reference Samples				0·371	269
Nitrogen prepared from $(NH_4)_2Cr_2O_7$				0·374	266

The abundance of ^{15}N in crude oil and coal of varying geological age has been investigated by Smith and Hudson.[53] They concluded from their results given in Table LXVI that there was no essential difference between the ^{15}N content in oil and coal and the normal content in atmospheric nitrogen.

Table LXVI.—Abundance Ratio of Nitrogen in Crude Oil and Coal

Sources of Nitrogen	Age 10^6 years	$^{15}N\%$	$^{14}N/^{15}N$
Crude oil, Leduc No. 1, Alberta, Canada	290	0·3715	268
Crude oil, Lloydminster No. 3, Alberta	105	0·3725	267
Coal, Atoka formation, Seminole, Okla., U.S.A.	230	0·3740	266
Coal, Frontier formation, Little Horse Creek, Wyo., U.S.A.	70–110	0·3687	270
Cylinder Nitrogen (Reference)	0	0·3705	269

Schoenheimer and Rittenberg[54] found that the concentration of the ^{15}N isotope in various natural amino acids was practically the same as that of atmospheric nitrogen. A few amino acids did, however, contain a slightly increased concentration. Arginine, for example, contained up to 0·378% of ^{15}N against 0·368% of ^{15}N in the atmospheric nitrogen used as a reference. Whether this difference was due to experimental error or whether it did demonstrate a real increase was difficult to decide. It is possible that in some chemical and biological reactions minute fractionation of the nitrogen isotope occurs.

Evidence for separation by diffusion of nitrogen isotopes in the atmosphere because of settling in the gravitational field of the earth has been presented by McQueen.[55] Air samples collected with high altitude rockets in the range from 40 km. to 60 km. above the surface of the earth were analysed, as was also a control sample at ground level. The results are given in Table LXVII.

Table LXVII.—Separation of ^{14}N and ^{15}N in the Upper Atmosphere

Altitude of Sample, km.	$^{14}N/^{15}N$ in Sample	% Separation
54·7–58·8	282·6	3·9 ± 0·4
53·6–57·7	279·4	2·7 ± 0·3
49·0–59·8	279·4	2·7 ± 0·5
50·4–53·3	274·1	0·4 ± 0·3
44·8–47·6	275·2	0·8 ± 0·3
41·4–44·9	< 274	< 0·3
0 (atmospheric nitrogen)	273	

$\%\ \text{Separation} = [(^{14}N_2/^{14}N^{15}N)\ \text{Sample} - (^{14}N_2/^{14}N^{15}N)\ \text{Ground}] \times 100.$

The observed separation was less than the calculated value, which was held to indicate possible mixing of the isotopes in the atmosphere especially below 40 km.

Hagelbarger *et al.*[56] and Jones *et al.*[57] have obtained results slightly different from those of McQueen; these indicate that even up to a height of 60 km. mixing in the atmosphere must occur.

In an investigation by Soloway,[58] no major difference in the ^{15}N content of nitrogen obtained from air, commercial nitrogen and a preparation of ammonium sulphate was obtained.

Reviewing the available evidence, McKellar[59] considers that no significant differences exist between terrestrial and stellar relative abundances of the isotopes of nitrogen. Bethe[60] has calculated that the $^{14}N/^{15}N$ ratio at the centre of the sun is 2×10^5 greater than the terrestrial ratio.

^{14}N has also been prepared artificially by the following reactions:

$^{16}O(d, \alpha)$, $^{11}B(\alpha, n)$ (Refs. 61–78)

and other similar reactions starting with a given isotope followed by bombardment with a particle necessary to produce the required transition to ^{14}N.

^{15}N has similarly been prepared as follows:

$^{14}N(d, p)$, $^{14}N(n, \alpha)$, etc. (Refs. 62, 65, 67, 79–92)

The process of formation of each isotope is indicated here and below in the conventional manner, i.e. the first symbol is the nucleon bombarded, the second is the bombarding particle or ray and the third is the particle or ray emitted along with the isotope formed (p = proton, d = deuteron, n = neutron, α = alpha particle (helium nucleus), β^+ = positron, β^- = electron, γ = gamma-ray photon.

Radioactive Isotopes of Nitrogen

The four radioactive isotopes of nitrogen have been made by nuclear reactions, as briefly summarized in Table LXVIII.

Table LXVIII.—Radioactive Isotopes of Nitrogen

Isotope	Process of formation	Properties			
		Half life	Atomic Mass	Particles Emitted (energies in MEV)	Refs.
^{12}N	$^{12}C(p, n)$ $^{14}N(\gamma, 2n)$ etc.	0·0125 sec.	12·0228	β^+(16·6)	93–95
^{13}N	$^{12}C(d, n)$ $^{14}N(\gamma, n)$ etc.	10·5 min., 9·93 min., 10·0 min. 9·2 min., 9·3 min., 9·9 min., 10·0 min.	13·01004	β^+(1·2)	96–143
^{16}N	$^{19}F(n, \alpha)$ $^{16}O(n, p)$ etc.	8 sec.	16·0062	β^-, 9·68 γ, 5·1	83 and 144–158
^{17}N	$^{14}C(\alpha, p)$ $^{18}O(\gamma, p)$ etc.	4·14 sec.	—	β^-	159–168

For further information on these isotopes the reader is referred to the radiochemical section in a later supplement.

Separation of the Nitrogen Isotopes

BY CHEMICAL EXCHANGE

Much work has been done on the method of chemical exchange. Equilibria for some of the simpler exchange reactions of nitrogen isotopes have been calculated by Urey[23] (Table LXIX) and Spindel[169] (Table LXX).

If A_1 and B_1 are two molecules containing ^{14}N, and A_2 and B_2 are two similar molecules containing ^{15}N, then the equilibrium constant for the reaction

$$aA_1 + bB_2 \rightleftharpoons aA_2 + bB_1$$

is expressible by the equation

$$K = (Q_{2A}/Q_{1A})^a/(Q_{2B}/Q_{1B})^b$$

where Q_{2A}, etc., refer to the partition functions for reactions between A_2 and ^{14}N, etc. The Q_2/Q_1 ratios can be calculated with the aid of the symmetry numbers and vibration frequencies of the molecules. Tables LXIX and LXX give values of Q_2/Q_1 for ions and molecules, as calculated by Urey and Spindel, together with the derived values of K for exchange reactions between pairs of these ions or molecules. Where K exceeds unity the ^{15}N isotope will concentrate in the compound listed on the left of the table and K will tend to ∞ as the temperature falls to 0°K.

Table LXIX.—Equilibrium Constant for Exchange Reactions between Pairs of Ions or Molecules Containing Nitrogen Isotopes

	$\frac{^{15}NH_4^+}{^{14}NH_4^+}$	$\left(\frac{^{15}N_2}{^{14}N_2}\right)^{1/2}$	$\frac{^{15}NH_3}{^{14}NH_3}$	$\frac{^{15}NO}{^{14}NO}$	$\frac{HC^{15}N}{HC^{14}N}$	$\frac{C^{15}N^-}{C^{14}N^-}$	Temp., °K.
Values of Q_2/Q_1	1·1184	1·0908	1·0768	$1{\cdot}073_8$	1·0736	1·0718	273·1
	1·1059	1·0814	1·0688	$1{\cdot}065_9$	1·0655	1·0641	298·1
	1·0721	1·0558	1·0472	$1{\cdot}044_0$	1·0439	1·0433	400
	1·0530	1·0410	1·0350	$1{\cdot}031_6$	1·0316	1·0315	500
	1·0409	1·0311	1·0271	$1{\cdot}023_8$	1·0238	1·0239	600

Continued overleaf

	$\frac{^{15}NH_4^+}{^{14}NH_4^+}$	$\left(\frac{^{15}N_2}{^{14}N_2}\right)^{1/2}$	$\frac{^{15}NH_3}{^{14}NH_3}$	$\frac{^{15}NO}{^{14}NO}$	$\frac{HC^{15}N}{HC^{14}N}$	$\frac{C^{15}N^-}{C^{14}N^-}$	Temp., °K.
			Values of *K*				
$\frac{^{15}NH_4^+}{^{14}NH_4^+}$	(1·000)	1·025	1·039	1·042	1·042	1·043	273·1
		1·023	1·035	1·038	1·038	1·039	298·1
		1·015	1·024	1·027	1·027	1·028	400
		1·012	1·017	1·021	1·021	1·021	500
		1·010	1·013	1·017	1·017	1·017	600
$\left(\frac{^{15}N_2}{^{14}N_2}\right)^{1/2}$		(1·000)	1·013	1·016	1·016	1·018	273·1
			1·012	1·015	1·115	1·016	298·1
			1·008	1·011	1·011	1·012	400
			1·006	1·009	1·009	1·009	500
			1·004	1·007	1·007	1·007	600
$\frac{^{15}NH_3}{^{14}NH_3}$			(1·000)	1·003	1·003	1·005	273·1
				1·003	1·003	1·004	298·1
				1·003	1·003	1·004	400
				1·003	1·003	1·003	500
				1·003	1·003	1·003	600
$\frac{^{15}NO}{^{14}NO}$				(1·000)	1·000$_2$	1·002	273·1
					1·000$_4$	1·002	298·1
					1·000$_1$	1·001	400
					1·000$_0$	1·000	500
					1·000$_0$	1·000	600
$\frac{HC^{15}N}{HC^{14}N}$					(1·000)	1·002	273·1
						1·001	298·1
						1·001	400
						1·000	500
						1·000	600

Table LXX.—Equilibrium Constant for Exchange Reactions between Pairs of Ions or Molecules Containing Nitrogen Isotopes

	$\frac{^{15}NO_3^-}{^{14}NO_3^-}$	$\frac{^{15}NO_2^{(a)}}{^{14}NO_2}$	$\frac{^{15}NO_2^{(b)}}{^{14}NO_2}$	$\frac{^{15}NO_2^-}{^{14}NO_2^-}$	$\frac{^{15}NO}{^{14}NO}$
Q_2/Q_1	1·169	1·089	1·109	1·072	1·066
			Values of *K*		
$\frac{^{15}NO_3^-}{^{14}NO_3^-}$	1·00	1·073	1·053	1·090	1·096
$\frac{^{15}NO_2^{(a)}}{^{14}NO_2}$		1·00	—	1·015	1·021
$\frac{^{15}NO_2^{(b)}}{^{14}NO_2}$			1·00	1·034	1·040
$\frac{^{15}NO_2^-}{^{14}NO_2^-}$				1·00	1·006
$\frac{^{15}NO}{^{14}NO}$					1·00

(*a*) Calculated on the assumption of a central force field.
(*b*) Calculated on the assumption of a valence force field.

The exchange of gaseous ammonia with solutions of ammonium salts has attracted a great deal of attention.[170–189] Urey and Thode[187–189] have reported separations of up to 75% of ^{15}N. The essential basis of their method is as follows: ammonium nitrate solution is fed continuously into the top of a column; it then passes to the bottom where it is converted completely into ammonia gas with sodium hydroxide and then returned upward through the column. As a result of isotope exchange ^{15}N tends to concentrate in the liquid phase, whilst the ammonia gas contains relatively more of the unwanted lighter isotope; there is thus a net transport of the ^{15}N constituent towards the bottom of the column where it concentrates. When the concentration of ^{15}N at the bottom reaches a value suitable for production a rich material is withdrawn continuously. A single column can be used conveniently for obtaining up to a ten-fold change in the ratio of the nitrogen isotopes. For high isotope concentrations the use of a uniform column throughout would require too long a wait for production. Thus a cascade arrangement embodying a series of columns progressively smaller as the concentration increases is often used. Urey and his co-workers using 3 units in cascade, each designed to effect a ten-fold enrichment, succeeded in producing a material containing up to 75% of ^{15}N at the rate of 1·3 g./day for exchange and tracer work.

In recent papers Spindel and Taylor[190] describe a method using the chemical exchange reaction:

$$^{15}NO + H^{14}NO_3 \rightleftharpoons {}^{14}NO + H^{15}NO_3$$

which can produce ^{15}N from 99·5% to 99·9% pure. They consider that the two-phase chemical exchange methods are more favourable than the Clusius thermal diffusion method (described below) for producing large quantities of ^{15}N. Although the NH_3–NH_4^+ exchange system has been used successfully for many years to produce up to 75% of ^{15}N, the NO–HNO_3 system is capable of producing ^{15}N at the same rate with considerably smaller equipment and with higher purity.

The exchange reaction between HCN and sodium cyanide (20% solution) has been investigated by Roberts *et al.*,[191] who found that ^{15}N concentrated in the liquid phase.

A somewhat different kind of chemical exchange reaction has been used by Urey and Taylor in their investigation of isotope separation by means of a zeolite column. By using a 10-metre column of zeolites, passing ammonium chloride solution through it and then converting the ammonium chloride into nitrogen, they produced a change of about 10%.[192, 193]

BY DIFFUSION

The Hertz diffusion method has been applied to the separation of nitrogen isotopes.[194–196] Riesenfeld[194] reports that with a 3-unit system the separation factor for ^{15}N is 4·5 and the yield per minute is 0·5 c.c.

The separation of pure $^{14}N^{15}N$ has been achieved by the thermal gas diffusion principle.[197–203] This method depends on the fact that with a mixture of gases contained in a vertical cylinder provided with a heater along its axis and having its wall externally cooled, a greater concentration of the lighter molecules in the mixture tends to be produced at the axis of the cylinder, and conversely a greater concentration of the heavier molecules at the wall. Hence, owing to convection up the axis and down the cooled outer wall, the lighter and heavier molecules tend to be concentrated at the top and bottom of the cylinder respectively so that separated fractions can be gradually drawn off. Clusius, Dickel and Becker[202] were able to obtain 800 c.c. of pure $^{14}N^{15}N$ by means of six units of total length 82 metres.

Pure $^{15}N_2$ cannot be prepared by the normal thermal diffusion method because of the resulting equilibrium among $^{14}N_2$, $^{15}N_2$ and $^{14}N^{15}N$ molecules. This difficulty was overcome by Clusius[204] by means of an electric discharge in the gas instead of using the heated wire. The electric discharge dissociates the molecules into atomic nitrogen. An apparatus consisting of 10 tubes having a total length of 27 metres resulted in the production of 99·8% pure $^{15}N_2$ after 25 days' enrichment. It would

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appear that this method and the chemical exchange method using NO–HNO_3, are the best available for the separation of substantially pure ^{15}N.

BY OTHER METHODS

A partial separation of the ^{15}N isotope has been achieved by the fractionation of liquid nitrogen at subatmospheric pressure.[205]

Other methods of separation include electrolytic separation[206] centrifugation,[207] distillation of HCN from solution in glacial acetic acid followed by passage of the HCN through a packed column counter-current to the incoming solution[208] and the exchange reaction of nitrogen isotopes on iron, tungsten and osmium catalysts.[209–211] For a more detailed account of some of the methods for separating the nitrogen isotopes the reader is referred to a review by Geller and Miklukin.[212]

USES OF NITROGEN ISOTOPES

As all the radioisotopes of nitrogen have a relatively short life, practically all the tracer work with nitrogen has been done with the aid of the stable nuclide ^{15}N. Both Urey's chemical exchange method and the Clusius thermal diffusion method (electric discharge) have been used for the separation of the ^{15}N isotope. Undoubtedly Taylor and Spindel's method will be of increasing importance.

Various syntheses in organic chemistry and mechanisms of some organic reactions have been investigated with the aid of the ^{15}N isotope.[213–230]

Clusius[231] has written a comprehensive summary of the characteristic features of ^{15}N chemistry which includes syntheses of $^{15}NH_3$, $H^{15}NO_3$, $H^{15}NO_2$; ^{15}N analysis by means of band spectroscopy; decomposition, ring formation and constitution of diazo compounds and azides; proof of the existence of the nitrate ion in liquid N_2O_4, etc. The reader should also consult the Russian paper[212] and the Japanese paper[174] previously mentioned for the further uses of ^{15}N in chemistry.

^{15}N has been extensively used in biochemical investigations; indeed many biologists consider that the most outstanding contribution to the understanding of life processes arising from the use of isotopes is that made by Schoenheimer, Rittenberg and co-workers.[232, 233] Since the work of Folin in 1905, most physiologists have distinguished two sources of nitrogenous compounds in the urine, as 'endogenous', i.e. derived from tissues, and 'exogenous', i.e. derived from food: they considered the main function of food is to supply the necessary energy for the various mechanical processes of the body whilst only a fraction of it is used in the synthesis of new tissue. This long-established concept of a static state of the organism was proved wrong by Schoenheimer and co-workers in 1938. With the aid of the ^{15}N isotope they demonstrated 'a dynamic state of the body constituents', in which there is a continual interchange between the structural units (e.g. amino-acids) of the nitrogenous compounds such as proteins and nucleic acids, which are already present in the animal body, and the structural units derived from proteins etc., during the digestion of food.

Further references to exchange reactions of nitrogen isotopes will be found in the section on the radiochemistry of nitrogen in a later supplement.

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SECTION III

NITRIDES

BY B. R. BROWN

INTRODUCTION

In this section the nitrides only of the metals are discussed; the nitrides of each of the non-metals will be reviewed under the appropriate element in later volumes.

The nitrides are usually divided into three classes: ionic, covalent and interstitial nitrides.

Ionic nitrides are formed by the elements of Groups I (M_3N) and II (M_3N_2), although in Group I lithium is probably the only alkali element to form a definite nitride of composition Li_3N. The compound Cu_3N is probably covalent. The nitrides of Group II elements are exemplified by beryllium nitride, Be_3N_2. Because of the doubt concerning the electronic structures of some nitrides, such as Ge_3N_4 and Th_3N_4, these are tentatively classified by some authors in the ionic class and by others in the covalent class.

Covalent nitrides are exemplified by Group III compounds, e.g., BN, AlN, GaN. Some Group IV nitrides, e.g., Sn_3N_4, Th_3N_4, Si_3N_4 are also usually included in this class.

Interstitial nitrides are numerous and are formed mainly by the transition metals. In these compounds the small nitrogen atoms occupy some or all of the interstices in the metallic lattices which are generally close-packed. The resulting structures may be the same as in such simple structures as the rock salt lattice, depending on the number of the interstices occupied by the nitrogen atoms and also on the type of interstice, i.e. whether tetrahedral or octahedral. Accordingly in this class are found such nitrides as ScN, LaN, CeN, PrN, TiN, ZrN and Fe_2N. Many of these nitrides have wide ranges and others very narrow ranges of homogeneity; an extreme example of this class is the nitride UN which has the stoicheiometric composition of the compound. It is interesting to note that the composition of interstitial nitrides with a narrow range of homogeneity is not determined by the valency of the metal, as is the case for some of the oxides of the transition metals which also have narrow ranges of homogeneity.

These interstitial structures are generally extremely hard substances, with high melting points. Their thermal and electrical conductivities are comparable with those of metals and at very low temperatures some of them become superconductors. These compounds are, therefore, of some industrial importance as well as of theoretical interest. Because of their similarity to the interstitial carbides (i.e. carbides of the transition metals of the 4th, 5th and 6th Groups of the Periodic Table, which have refractory properties), the interstitial nitrides are classified with these substances in the term 'hard metals', i.e. compounds which behave like metals in most respects but are in fact much harder.

The first effort to systematize the 'hard metals' was made by Hägg[1, 2] from an investigation of the hydrides, borides, carbides and nitrides of some of the transition elements; all these compounds exhibit strongly metallic properties, whilst the corresponding compounds formed with other metals are non-metallic in character.

Hägg observed that for the binary interstitial compounds of the transition elements if the ratio $r_x:r_m$ is less than 0·59 the structure is simple ('normal'), with the non-metallic atoms occupying the interstices of the metal lattice. Furthermore the metallic lattice usually consists of the metal atoms simply arranged either in cubic or hexagonal closest packing, whilst body-centred cubic and simple hexagonal arrangements are rarely encountered in such substances. Where the radius ratio is greater than the critical value of 0·59, many of the compounds are still metallic in character, but their structures are more complex, the degree of complexity increasing with decrease in the size of the metal ion. It is also important to realize that an essential part of Hägg's hypothesis is that in most compounds of this type the metallic lattice in the so-called 'normal' interstitial phases is identical with the original lattice of the metal. According to Rundle[3] exactly the opposite is true, the arrangement of the metal atoms in the interstitial compounds (MX) differing from the original metal lattices. In the light of later work it seems that Hägg's rule of the limiting radius ratio is valid only for the carbides.

Hägg[4] has recently suggested that the definition of 'hard metals' should be broadened to include interstitial oxides, double oxides, phosphides, sulphides and nitride-oxides of the transition metals. Also now included in this class are interstitial silicides of the transition metals.

Schwarzkopf[5, 6] points out that from a practical viewpoint the metallic character of the phases formed by these interstitial compounds is more important than the structure of the crystal lattices; accordingly classification of interstitial compounds as metals and non-metals should be based on the formation of metallic phases rather than on their crystal structure and dimensional relationships. It is a logical step, therefore, to enquire into the nature of bonding arrangements in the crystal lattices. Probably the most useful interpretation (as far as nitrides are concerned) of the observed facts with reference to hard metal structures has been put forward by Rundle,[3] whose theory is concerned only with electron deficient compounds of the MX type (i.e. monocarbides, mononitrides and monoxides). He emphasizes that any satisfactory theory of bond structure must give an interpretation of two important aspects of these compounds, viz. (1) that most interstitial compounds of the MX type have the rock salt structure irrespective of whether the metal from which the interstitial phase is derived has a cubic close packed structure or not, and (2) that all interstitial phases are hard and have very high melting points. Considering these factors Rundle asserts that they indicate strong metal to non-metal bonding and furthermore that the bonding is octahedral, six equal bonds being directed from the non-metal towards the corners of an octahedron.

In an earlier discussion of these compounds, Pauling had considered that since the maximum covalence of nitrogen (and carbon) is 4, the bonding arrangement is such that resonance of 4 covalent bonds amongst 6 positions must occur. Rundle using Pauling's basic concepts goes further and postulates the existence of so-called 'half bonds' in such compounds. Such 'half bonds' are formed by elements of the first period using two *p* orbitals to form two bonds at 180°, but only one electron pair is associated with the two bonds. It is important to note that each of the two electrons is involved in resonance between two bonds and hence such bonds differ from the so-called electron bond.

Stronger octahedral bonding can be achieved also by using two equivalent *sp*-orbitals to form electron pair bonds and then hybridizing with four half bonds formed by the remaining two *p*-orbitals. Such half bonds, which amount to a system of resonating bonds, would explain hardness, high melting point, electrical conductivity, etc., and also the metallic character by analogy with the resonating structure of metals.

Schwarzkopf considers that Rundle's theory is only part of a much more general theory applicable to all interstitial substances in the 'hard metal' category. Some aspects for instance are best considered from the viewpoint of resonating bond structures (involving essentially homopolar forces), whilst other aspects are best interpreted on the basis of ionic structures (involving essentially heteropolar forces).

In addition to the references mentioned above[1–6] the reader is directed to general papers[7–57] some of which review methods of preparation, chemical and physical properties and uses of the nitrides.

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NITRIDES OF GROUP I METALS

Lithium Nitride

Duparc *et al.*[1] prepared lithium nitride, Li_3N, by passing pure nitrogen at atmospheric pressure over lithium at 400° to 450°C. If the lithium is prepared in a very fine state of subdivision by the reduction of Li_2O with powdered aluminium, a more active form of the nitride is obtained, especially when the reduction with aluminium is carried out in two successive operations. Lithium reacts with electrically activated nitrogen to give a small yield of the nitride.[15] Lithium nitride crystallizes in the hexagonal system[2] with unit cell dimensions $a = 3{\cdot}658$ A., $c = 3{\cdot}882$ A. Brill[3] has suggested that there may be two modifications of lithium nitride.

In a study of the electrical conductivity of the solid and liquid nitride, Gallais and Masdupuy[4] found that up to 360° the nitride crystals have almost no conduction. Between 360° and 550°C. they display the characteristics of crystalline conduction represented by the equation:

$$X = 0{\cdot}0528\, e^{-6196/T} + 4{\cdot}3 \times 10^7\, e^{-21700/T}$$

Above 550° the conductivity continues to increase and at the melting point $X = 8{\cdot}2 \pm 0{\cdot}3$. Above 550° decomposition takes place, nitrogen being evolved. It was concluded that Li_3N is an ionic compound containing Li^+ and N^{3-} ions.

Neumann *et al.*[5] found that the heat of formation of Li_3N is $47{\cdot}166 \pm 0{\cdot}308$ kcal./mole. Satô[6] measured the specific heat of lithium nitride over the temperature range 0–503°C., the data conforming to the equation:

$$C_p = 0{\cdot}5127 + 7{\cdot}2226(10^{-4})t - 1{\cdot}193(10^{-7})t^2$$

Kelley[7] calculates that the entropy and free energy of formation are $\Delta S_{298{\cdot}1} = -34{\cdot}0$, $\Delta F^{\circ}_{298{\cdot}1} = 37{\cdot}330$ kcal./mole respectively. Similar thermodynamic values are given by Brewer *et al.*,[8] who report also a decomposition temperature of 548°C.

The activation energy of adsorption of nitrogen on lithium is 47 kcal./mole.[9]

When heated in nitrogen with varying amounts of lithium nitride, cobalt takes up nitrogen to the limiting composition Co_3N. *X*-Ray examination of the crystalline solid solution shows that cobalt replaces up to half of one of the three lithium atoms in the lithium nitride lattice (17 atom-% cobalt). The *c* axis diminishes whilst the *a* axis increases with increasing cobalt content; the volume of the unit cell also decreases. Corresponding work with nickel and copper gives similar results, solid solutions with compositions $(LiNi)_3N$ and $(LiCu)_3N$ being formed; the maximum nickel content is 21 atom-% and correspondingly 10 atom-% for copper. It is assumed that the heavy metal enters the solid solution as univalent positive ions, the volume contraction being due to polarization by an ion with 16–18 outer electrons.[10]

The compound LiMgN is prepared by heating Li_3N with Mg_3N_2 or magnesium in a current of nitrogen or ammonia, or by heating LiMg in a current of ammonia. Similarly LiZnN is prepared by heating a mixture of Li_3N and Zn_3N_2 in a current of ammonia. The former compound, LiMgN, is a light red-brown substance with density 2·41; the latter, LiZnN, is black with density 4·56–4·61. LiMgN is stable for a short time in a current of nitrogen at 1100°C.; LiZnN decomposes at 500° in a stream of nitrogen or hydrogen. Below 500°C. dry hydrogen has little effect on LiMgN, but ammonia gives $LiMgN{,}0{\cdot}95NH_3$ which is stable below 450°C. Both ternary nitrides hydrolyse easily and dissolve readily in dilute acids.[10]

The ternary nitride Li_3AlN_2 is prepared by heating mixtures of Li_3N with aluminium or Li_3Al with nitrogen or Li_3N with AlN. Li_3GaN_2 is prepared similarly. Li_3AlN_2 is a light grey substance with density 2·33. It is stable at 1000°C. in an atmosphere of nitrogen, but takes up ammonia at 350° to give $Li_3AlN_2,1{\cdot}8NH_3$. The less stable Li_3GaN_2 is light grey with density 3·35. It decomposes when heated to 800°C. in nitrogen. It also combines with ammonia. Both Li_3AlN_2 and Li_3GaN_2 are easily hydrolysed and decomposed by acids.[11, 12]

When finally divided iron and lithium nitride are heated in nitrogen to 280–730°C. a complex nitride with the composition Li_3N,FeN is formed; decomposition commences at 730° and the reaction is reversed on cooling.[13]

Sodium Nitride

Nitrogen activated electrically at low pressure reacts vigorously with sodium to give sodium nitride; sodium azide is not formed under these conditions. If, however, the activated nitrogen reacts for a longer time the nitride is converted into the azide.[14] In the earlier work of Moldenhauer and Möttig[15] it was stated that sodium nitride is not formed under these conditions. When electrically activated nitrogen reacts with potassium, the nitride can barely be detected,[14] the azide being formed after only 30 sec. Ribidium and caesium act in the same way as potassium.[14] If sodium azide and sodium are dissolved in liquid ammonia and the solution is evaporated, as much as 50% of the sodium azide is converted into the nitride. Probably the formation of the nitride is a stage in the decomposition of sodium azide into sodium and nitrogen.[14]

The colour of sodium nitride varies with temperature; at −180° it is orange, at 20° vermilion, at 100° dark red, at 300°C. black. At 150° it decomposes appreciably; at 200° it decomposes in about 1 hour and at 350°C. in a few minutes. The density is about 1·7. The chemical properties resemble those of sodium. With water, sodium hydroxide and ammonia are formed, and correspondingly with ethyl alcohol sodium ethoxide and ammonia are produced. Hydrogen reduces it at about 120° to sodium hydride and ammonia. It is stable in dry oxygen at room temperature, but burns in it at higher temperatures. It reacts slowly with ammonia to give sodium amide. At −60°C. the red nitride turns blue in ammonia owing to the formation of an ammoniate; further reaction eventually occurs to give the amide.[14]

The specific heat of sodium nitride over the temperature range 0°–100°C. is 0·2934.[16]

Copper Nitride

Copper reacts with neither nitrogen nor ammonia at temperatures up to 900°C.,[17] but Juza and Hahn[18] have prepared analytically pure copper nitride, Cu_3N, by heating copper fluoride at 280° in ammonia. Cathodic vaporization of copper in an atmosphere of nitrogen at reduced pressure (0·5–1 mm. Hg) gives a black iridescent deposit of Cu_3N, which has properties similar to those of the nitride prepared by conventional chemical methods.[19] It is a dark green powder stable in air at room temperature. It is decomposed by dilute mineral acids and concentrated hydrochloric acid with the formation of ammonium salts. With concentrated sulphuric and nitric acids it reacts violently. Dilute and concentrated alkalis have little action on it. When heated to 230°C. in hydrogen it begins to decompose, whilst at 300°C. it dissociates in an atmosphere of nitrogen. At 300°C. it begins to decompose in oxygen, and combustion occurs at 400°C. In ammonia the nitride begins to decompose at 330°C. When heated in vacuo it decomposes at 450°C.

X-Ray analysis shows that copper nitride has a cubic structure with 1 molecule in the unit cell; the length of side of the unit cube is $a = 3{\cdot}80 \pm 0{\cdot}004$ A.[20] The structure corresponds to the DO_9 type; it is therefore anti-isomorphous with ReO_3.[21] The density is 5·84 g./c.c.[18] The specific heat over the temperature range 0°–100° is 0·1059,[22] and the heat of formation is −17·8 kcal./mole.[18] The magnetic susceptibility extrapolated to infinite field strength is $(0{\cdot}5\text{–}0{\cdot}05)10^{-6}$.[23]

Silver Nitride

Cathodic sputtering of silver in nitrogen at reduced pressure results in the fixation of very little nitrogen and it is doubtful whether any silver nitride is formed. Gold gives similar results.[24] In the preparation of silver nitride, Ag_3N, by precipitation from ammoniacal silver oxide solution by ethyl alcohol or acetone, the product contains variable amounts of silver and silver oxide. Silver nitride free from silver oxide, but containing small amounts of silver and silver chloride, is obtained by heating concentrated ammoniacal silver chloride with solid potassium hydroxide until evolution of ammonia ceases. The thoroughly washed product must be stored under water and even so it is sensitive to touch; the dried product explodes readily. The nitride is insoluble in cold alkalis. It decomposes slowly at 25°C. in moist or dry air and rapidly in vacuo. *X*-Ray analysis shows it to have a face-centred cubic structure with $a = 4{\cdot}369$ A.; there are 1·3 molecules in the unit cell. The nitrogen atoms probably occupy octahedral holes in the face-centred cubic lattice of silver atoms.[25]

Silver nitride, deposited as a black powder or as a shiny layer, explodes when illuminated with an electron flash of sufficient energy.[26, 27] From a determination of the heat of solution of the nitride in sulphuric acid, the molal heat of formation of Ag_3N is calculated to be $-61{\cdot}0$ kcal./mole.[25]

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NITRIDES OF GROUP II METALS

Beryllium Nitride

Nitrogen appears to have a negligible solubility in beryllium. The nitride Be_3N_2 has been prepared[1] by passing nitrogen or ammonia over the metal at temperatures

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between 800° and 900°C. for periods of 5 to 17 hours. It can be obtained also by treating beryllium chips with nitrogen containing 3–5% of hydrogen at 1150° for 4 hours and then at 1250° for an additional 12 hours.[1] A phosphorescent form of beryllium nitride can be prepared by treating a mixture of beryllium and 30% of aluminium oxide with ammonia for 5 hours at 1050°C., the aluminium acting as a catalyst.[3, 4, 5] The product shows blue luminescence after exposure to a mercury arc lamp.

Beryllium nitride has a cubic lattice (Th_2O_3 type structure) with a lattice parameter of $a = 8{\cdot}14$ Å.[1] or 8·13 Å.[6]

On heating beryllium nitride to 2000°C. in vacuo volatilization occurs, and it apparently does not dissociate appreciably below its melting point (2200°C.).[1]

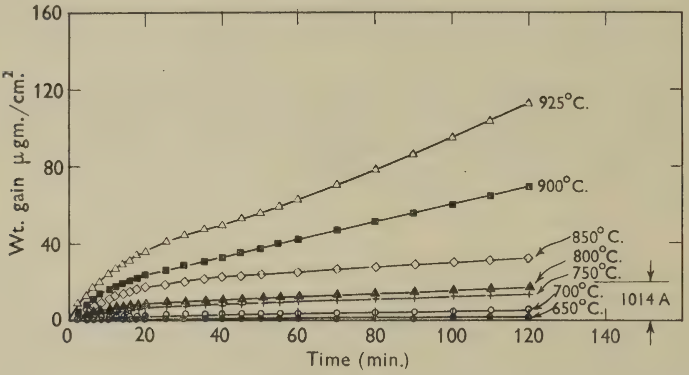

FIG. 1.—Reaction of beryllium with nitrogen (7·6 cm.); effect of temperature

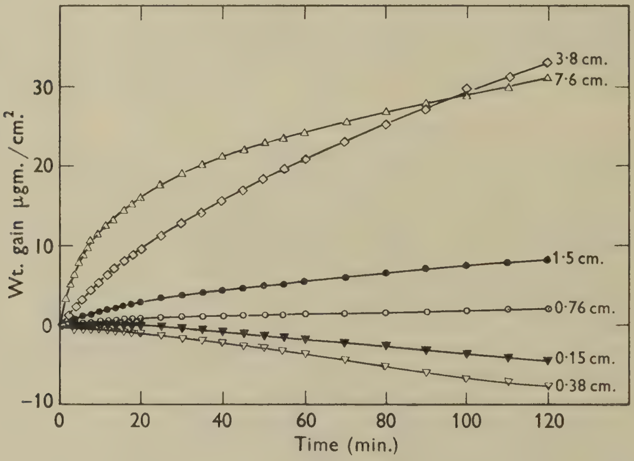

FIG. 2.—Reaction of beryllium with pure nitrogen at 850°C.; effect of pressure

The heat of formation of beryllium nitride as determined by two different methods is $\Delta H = -133{\cdot}5$ kcal./mole[7] and $-135{\cdot}3$ kcal./mole.[8] Kelley[9] accepts the former value and estimates that the entropy is $S_{298{\cdot}1} = 12$ e.u., which gives for the entropy of formation a value of $\Delta S_{298{\cdot}1} = -40{\cdot}6$ e.u. and free energy of formation of $\Delta F^{\circ}_{298{\cdot}1} = -121{\cdot}4$ kcal./mole.

The reaction of nitrogen with beryllium over the temperature range 600°–925°C. has been studied using the vacuum micro-balance method.[10] Figs. 1 and 2 show the effect of temperature and pressure respectively on the reaction. The data can be fitted to the parabolic rate law, and some values of the constant K in the equation $w^2 = Kt + C$ (where w = the weight absorbed, K and C are constants and t is time) are given in Table I.

Table I.—Parabolic Rate Law Constants, Entropies, Energies and Free Energies of Activation for the Reaction of Nitrogen and Beryllium

Temp., °C.	K(cm.^{2}/sec.)	ΔS g.-cal. per mole °C.	E g.-cal. per mole	$T\Delta S$ g.-cal. per mole	ΔF g.-cal. per mole
650	$2{\cdot}95 \times 10^{-16}$				
725	$4{\cdot}90 \times 10^{-16}$	13·1	75,000	13,080	61,900
850	$2{\cdot}86 \times 10^{-14}$	12·3	75,000	13,850	61,150
925	$6{\cdot}01 \times 10^{-14}$	14·3	75,000	16,750	58,250

The rate of the reaction of nitrogen with beryllium was shown to be somewhat slower than the corresponding oxygen reaction. It was also established that nitride films, like oxide films, have a considerable effect on the vapour pressure of beryllium.

The effect of neutron irradiation on beryllium nitride has been reported.[11]

Magnesium Nitride

Magnesium nitride, Mg_3N_2, can be prepared in the laboratory by passing nitrogen, dried by passage through soda-lime and then concentrated sulphuric acid, over magnesium powder heated to 300–700°C. for about two hours, the yield being 60 to 90%.[12] Metal-free Mg_3N_2 (containing 0·9% MgO) has been prepared by maintaining an atmosphere of nitrogen over filings of 99·9% magnesium in an iron boat at 650–700°C. for 3–4 hours and subsequently raising the temperature to 950° for 12 hours.[13]

Pure Mg_3N_2 for magnetic measurements is prepared by initial sublimation of the magnesium at 700° in vacuo followed by filtration of the vapour and then heating the magnesium to 850° in a current of ammonia, the product being then heated to 250°C. in vacuo.[14]

Magnesium nitride is formed in the reaction between chromic oxide and magnesium when heated in the presence of air.[15]

Very pure magnesium nitride is formed by placing pieces of magnesium metal in a reaction vessel, evacuating to remove air and moisture, and then heating the magnesium above its sublimation temperature but below its melting point; a limited amount of nitrogen (or ammonia) is admitted to initiate the nitriding at the surface of the magnesium, and complete conversion of all the metal to the nitride is then achieved by heating to a temperature sufficient to cause sublimed magnesium to break through the surface coating of Mg_3N_2 and gradually admitting additional amounts of nitrogen.[16]

Magnesium nitride, useful as a dehydrating agent in inorganic reactions and organic syntheses and in rubber compounding, is obtained by starting with finely divided magnesium (produced by vaporizing magnesium metal, shock-chilling and recovering the solid condensate) and treating this with nitrogen or ammonia in a steel vessel heated to 350–400°C.[17, 18]

Magnesium nitride has a body-centred cubic lattice of the Mn_2O_3 type with 16 molecules to the unit cube; the side length is reported as $a = 9{\cdot}93$ A.[19, 20] and 9·97 A.[21]

Mitchell has obtained three allotropic modifications, with transition temperatures and heats of transition respectively of 823 ± 3°K., and 220 g.-cal./mole for $\alpha \rightleftharpoons \beta$; 1061 ± 5°K. and 260 g.-cal./mole for $\beta \rightleftharpoons \gamma$.[13]

The mean value of the molecular susceptibility χ_m is $-44{\cdot}2\times10^{-6}$. Following the method of Klemm for calculating the ionic susceptibility of crystals the magnetic susceptibility of the nitrogen ion in Mg_3N_2 is calculated to be $-18{\cdot}1\times10^{-6}$ and that of the magnesium ion to be $2{\cdot}63\times10^{-6}$. The molecular susceptibility is approximately 35% less than the value calculated from the sum of the susceptibilities of the gaseous ions ($-67{\cdot}7\times10^{-6}$). Comparison of the molecular susceptibilities of Mg_3N_2, Zn_3N_2 and Cd_3N_2 shows that the polarizing action of the metal ion decreases from magnesium to zinc to cadmium.[14]

Satô[22] has found that the specific heat of magnesium nitride over the temperature range 0–418°C. conforms to the equation

$$C = 0{\cdot}226+2{\cdot}462\times10^{-4}t-3{\cdot}693\times10^{-8}t^2$$

Mitchell[13] gives the following equations for the heat contents ($\Delta H = H_T - H_{298{\cdot}1}$) of the three forms of magnesium nitride in g.-cal./mole.

$$\begin{aligned}\Delta H_\alpha &= -7125+22{\cdot}81T+3{\cdot}65\times10^{-3}T^2\\ \Delta H_\beta &= -10{,}020+29{\cdot}60T\\ \Delta H_\gamma &= -9695+29{\cdot}54T\end{aligned}$$

From these data the specific heats and entropies were calculated over the range 350–1200°K. From the heat of solution of magnesium nitride in hydrochloric acid the heat of formation of the nitride is calculated to be

$$\Delta H_{298{\cdot}16} = -110{\cdot}240\pm0{\cdot}275 \text{ kcal./mole}^{13}$$

Other workers give values for the heat of formation of $-116{\cdot}0$[8] and $-115{\cdot}18$ kcal./mole.[7] Kelley[9] accepts the latter value as being correct and for the free energy of formation gives a value of

$$\Delta F^\circ_{298} = -100{\cdot}7 \text{ kcal./mole}$$

Mitchell[13] calculates the heat of formation of the γ nitride to be:

$$\Delta F^\circ = -224{,}240+189{\cdot}67T+5{\cdot}00\times10^{-4}T^2+8{\cdot}13T\ln T \text{g.-cal./mole}$$

The dissociation pressure is calculated to be 1 atm. at 1790°K.[13]

Magnesium nitride is strongly fluorescent, bright orange, when illuminated with ultra-violet light.[13]

With the oxides and chlorides of aluminium, titanium and chromium, magnesium nitride reacts to give the corresponding nitride. It reduces the oxides of silver, tin and lead to the metal, and lead sulphate is reduced to lead sulphide.[23] The nitride reacts with alkyl halides when heated for some hours at about 200°C. in a sealed tube; e.g., methyl iodide (MeI) is converted to Me_4NI.[24]

Calcium Nitride

Calcium nitride (Ca_3N_2) can be prepared by substituting nitrogen for phosphorus in phosphides,[33] the phosphides being obtained from phosphates by reduction with carbon. This method can be used also for the other alkaline earth nitrides.

At 400–440°C. the reaction between pure calcium and pure nitrogen takes place in three stages[25]; (*a*) a fast reaction involving only atoms of calcium on the surfaces of the crystal; (*b*) a very slow reaction involving atoms beneath the thin skin of calcium nitride; (*c*) a second fast reaction after the skin of nitride has reached a definite thickness. Oxygen prevents nitrogen from reacting with a fresh surface of calcium, but a skin of the nitride once having formed the metal is protected against oxygen and the nitrogen reaction proceeds. The metals lithium, sodium, potassium, and probably also rubidium and caesium influence the reaction greatly, not as catalysers but rather as 'reaction exciters'.

Hartmann and Fröhlich[26] found that pure nitrogen shows practically no reaction with pure calcium at 400°C., because the reaction ceases with the formation of a thin brown layer of nitride over the calcium. Furthermore on activation of the pure calcium with sodium (less than 1%) calcium nitride is formed. Further work has shown that sodium hydroxide as well as sodium favours the formation of the nitride.[27–31] The effect of alkali metals on the rate of reaction is explained by Franck and Bodea on the basis of two crystalline forms of calcium metal.[32]

The kinetics of the reaction of calcium with nitrogen have been studied and it has been found that this reaction is autocatalytic at temperatures below but not above 430°C.[34] The induction period is given by $1/(Ap)$ where A is a function of temperature and p is the initial pressure of nitrogen. When the area of the calcium nitride interface is constant the reaction is of the first order. The induction period t falls rapidly from 150 sec. to 3 or 4 sec. as the temperature rises from 330° to 480°C. The rate of reaction r is a maximum at 500°C. The activation energy E calculated from the equation $t = ce^{E/RT}$ where c is a constant, 31·5 kcal./mole; the value of E calculated from r is 23·0 kcal./mole. The difference is attributed to the energy of formation of the nascent phase. The reaction has two critical temperatures as a result of the formation of intermediate compounds. Furthermore the more finely divided is the calcium the more rapid is the reaction.[35] The nitride may be prepared in a state of fine subdivision by dissolving it in liquid ammonia and decomposing the resulting hexamine at low temperature in vacuo.[35] The calcium nitride formed by heating calcium in nitrogen for a long time at 1200° is citron yellow; it is black below 350°, blue-black up to 600°, reddish-brown up to 850°, greenish up to 1100° and yellow above 1150°C.[35]

It has been found[31, 36] that very small amounts of argon inhibit the reaction between calcium and nitrogen. Cooling curves of the system calcium–calcium nitride in an atmosphere of argon[37] show arrests at 780° and 809°, but it is not known which arrest corresponds to the calcium nitride eutectic, which contains 3–4% of nitride. The melting point of calcium nitride is 1195 ± 1°.

Two modifications of calcium nitride have been reported, viz., a cubic form with 16 molecules in the unit cell and a second form which is not cubic.[6]

A pseudo-hexagonal form of calcium nitride has been obtained[26] at 300° with $a = 3{\cdot}533$, $c = 4{\cdot}11$ Å.; on heating to 500° this form changes irreversibly to the cubic form (Mn_2O_3,D_{53} type) with $a = 11{\cdot}38$ Å.

Other workers[38] have observed three forms of Ca_3N_2: (1) a black nitride obtained below 600–750°; (2) a brown nitride obtained at higher temperatures; and (3) a yellow nitride which sublimes above 1150–1200°C. Form (1) can be changed into (2) irreversibly. The structure of (2) is similar to that of magnesium nitride, Mg_3N_2, i.e. cubic face-centred with $a = 11{\cdot}40$ Å. (16 molecules of Ca_3N_2 per unit cell), the calculated density being 2·64 g. per c.c. as compared with the observed value of 2·54 g. per c.c. (1) is either hexagonal or tetragonal with six or eight molecules to the unit cell; the density is either 2·66 or 2·69 g. per c.c.

Calcium nitride when heated in hydrogen gives a clear greenish-yellow compound with an *X*-ray diagram like that of CaO (cubic face-centred, $a = 5{\cdot}006$ Å.). This is presumed by Franck[38] to be CaNH; it has 4 molecules of CaNH to the unit cell and density 2·893 g. per c.c.

The heat of formation of calcium nitride is given[39] as 102·6 ± 1 kcal./mole. From this the entropy is estimated to be $S_{298{\cdot}1} = 25{\cdot}4$ e.u., which makes $\Delta S_{298{\cdot}1} = -50{\cdot}2$ e.u. for the entropy of formation from the elements.[9]

The specific heat over the temperature range 0–500°C. is given by the equation[40]:

$$C = 0{\cdot}1817 + 1{\cdot}273 \times 10^{-4}t + 1{\cdot}388 \times 10^{-8}t^2$$

Using this equation the heat of formation at 25°, calculated from the dissociation pressure and the Nernst heat theorem, is 108·200 kcal./mole

Calcium nitride is useful as a desulphurizing agent for blast furnace metal.[41] Analytical methods for determining calcium nitride in calcium cyanamide have been described.[42, 43]

Strontium Nitride and Strontium Pernitride

The nitride of strontium, Sr_3N_2, is well established (Mellor, VIII, 102). The heat of formation is $\Delta H = -91{\cdot}400$ kcal./mole and the free energy of formation is $\Delta F^{\circ}_{298\cdot1} = -76{\cdot}230$ kcal./mole.[9] Unlike the nitrides of magnesium and beryllium, strontium nitride does not possess a cubic structure.[6]

The alkaline earth amides when heated in a high vacuum give red-brown products having the composition M_3N_4 with MNH as an impurity.[44] These pernitrides react with dilute acid thus:

$$Sr_3N_4 + 8HCl \rightarrow 3SrCl_2 + 2NH_4Cl + N_2$$

Attempts to determine the structure of the pernitrides by means of *X*-rays were unsuccessful.

From a consideration of enthalpies of formation Ariya and Prokofeva[45] concluded that only barium could form higher nitrides; they therefore repeated the foregoing work. $Sr(NH_2)_2$ prepared from metallic strontium and liquid ammonia and containing only a trace of $Sr(OH)_2$ was decomposed at 400–500°C. in a vacuum; the product exhibited the properties observed by Hartmann but on treatment with dilute hydrochloric acid the gas formed was hydrogen and not nitrogen; accordingly the compound could not be a higher nitride of strontium. Later work by these authors confirmed the existence of the nitride Sr_2N.[46]

Ehrlich and Hein[47] claimed to have prepared specimens of the pernitride Sr_3N_4 and used them in magnetic measurements at 90° to 673°K. Their results indicate that this compound is salt-like in structure and contains N_2^{3-}. Two possible explanations are advanced to account for the low magnetic moment: (1) in contrast to NO the coupling of the orbit and spin moments which are anti-parallel to each other is only partly disturbed; (2) there is a temperature-sensitive equilibrium between diamagnetic N_4^{6-} and a paramagnetic $2N_2^{3-}$ ion which lies strongly on the side of the dimeric molecular ions. It seems that there is little likelihood of settling this question by *X*-ray analysis because of the strong screening effect.

The heat of formation of strontium nitride, Sr_3N_2, is $\Delta H = 91{\cdot}4$ kcal./mole, and the free energy of formation is $\Delta F^{\circ}_{298\cdot1} = -76{\cdot}230$ kcal./mole.

Barium Nitride

The nitride of barium, Ba_3N_2, is well known (Mellor, VIII, 102); and the existence of Ba_2N has been established.[45, 46]

The heat of formation of Ba_3N_2 is $\Delta H = -89{\cdot}9$ kcal./mole, and the free energy of formation $\Delta F^{\circ}_{298\cdot1} = -72{\cdot}790$ kcal./mole.

Ba_3N_2, like Sr_3N_1, but unlike Ca_3N_2, does not possess a cubic structure.[6]

When barium nitride is mixed with natural graphite and heated to 850–1180°C., in a closed vessel the major product is barium cyanide, the yield depending on the temperature.[48]

Nitrides of Zinc, Cadmium and Mercury

The solubility of nitrogen in zinc is almost negligible.[49] An electric arc between two zinc electrodes in a nitrogen atmosphere produces zinc nitride, Zn_3N_2.[2] The products of condensation of zinc vapour in nitrogen or of passing ammonia through molten zinc at 600°C. contain only traces of zinc nitride; yields of 5–40% are obtained from zinc dust and ammonia at 550°C.[51] Juza *et al.*[52] obtained zinc nitride by the reaction of ammonia with zinc and also by the thermal decomposition of zinc amide, $Zn(NH_2)_2$. As prepared from the amide it is a finely divided black powder which decomposes slowly in air. The product from zinc and ammonia is greyish black and more stable in air.

The product from the amide is easily soluble in 2N-HCl and H_2SO_4, and rapidly soluble in concentrated sulphuric acid, evolving nitrogen: in 2N. sodium hydroxide it dissolves slowly when cold but vigorously when hot, ammonia being evolved.

When heated in oxygen at 400°C. its surface becomes lighter, and at 730°C. it is completely oxidized. When the nitride is heated in hydrogen, ammonia begins to form at 400° and is evolved very rapidly at 600°: it decomposes in ammonia at temperatures over 600° and in nitrogen at somewhat lower temperatures.[52]

Zinc nitride, like cadmium nitride, is anti-isomorphous with Mn_2O_3 (type $D5_3$) with $a = 9{\cdot}74_3 \pm 0{\cdot}005$ A. It has 16 molecules in the unit cell and density 6·40 g. per c.c.[56] The heat of formation is 24·06 (±28%) kcal./mole. The dissociation constant for the range 37–537° has also been calculated.[51]

The mean specific heats of zinc nitride over the temperature range 0–419°C. conform to the equation[53]:

$$C_p = 0{\cdot}1142 + 8{\cdot}926 \times 10^{-5}t + 1{\cdot}151 \times 10^{-8}t^2$$

Cadmium nitride has been prepared by heating the amide, $Cd(NH_2)_2$, for 36 hours at 180°C. in vacuo. It is obtained as a fine black powder which is decomposed by moisture and oxidized by air. With dilute acids and bases it reacts explosively. The heat of formation is 38·6 ± 0·4 kcal./mole. Like zinc nitride it is anti-isomorphous with Mn_2O_3 (type $D5_3$), with $a = 10{\cdot}79 \pm 0{\cdot}02$ A.; the unit cell contains 16 molecules and the density is 7·67.[56]

Streaming nitrogen activated by electric discharge reacts with mercury to produce at 2 mm. Hg pressure a compound which is considered to be a mercury nitride, Hg_3N. It is decomposed by water and sodium hydroxide with formation of ammonia.[54] Heating under 2 mm. Hg pressure at 95–100°C. brings about decomposition.[54]

Mercuric nitride in liquid ammonia solution reacts with hydrazobenzene yielding azobenzene.[55]

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NITRIDES OF GROUP III METALS

Aluminium Nitride

PREPARATION

Nitrogen is almost insoluble in both liquid and solid aluminium.[1, 2, 3] The rate of nitrogen adsorption increases with temperature[1]; just above the melting point the adsorption stops after a short time, whilst at higher temperatures it continues. When aluminium has once adsorbed nitrogen it is impossible to degas it. Between 700° and 1000° aluminium nitride, AlN, is formed on the surface and retards further adsorption; this nitride layer is so thin that it cannot be detected under the microscope.

A refractory containing aluminium nitride is produced by heating a mixture of aluminium, carbon and calcium fluoride or sodium aluminium fluoride to 1000°C. in an atmosphere of nitrogen until the mixture contains 60–85% of AlN: the carbon prevents formation of an undue amount of alumina, and the cryolite or calcium fluoride forms a strong binder for the aluminium nitride and residual carbon. A vitrified refractory consisting essentially of AlN (15–50%) and Al_2O_3 (85–50%) is made by fusing these materials together in an electrically heated graphite crucible; temperatures of 2000–2300° are used, i.e. about 100° above the softening or melting point of the refractory prepared. The temperature is not allowed to exceed 2300°C. because of thermal decomposition of the nitride. Refractories containing the larger quantities of AlN melt at about 2200°C.; the melting point of substances containing smaller quantities of AlN is approximately 1900°C.[4]

If alumina is heated with a small amount of zinc chloride, ferric oxide and carbon in an atmosphere of nitrogen, the product contains about 60% of aluminium nitride.[5] A continuous method of making aluminium nitride from aluminium oxide, carbon and nitrogen is reported.[6]

Direct nitrogenation of silico-aluminium, containing very little iron or titanium, produced aluminium nitride.[7] The nitride can also be prepared by passing ammonia over powdered aluminium at 800–900°C.[8]

On treating the fused monammine of $AlCl_3$ with aluminium, hydrogen is evolved and a complex compound is formed according to the equation:

$$AlCl_3,NH_3 + Al \rightarrow AlCl_3,AlN + \tfrac{3}{2}H_2$$

The complex is so stable that complete decomposition does not take place even when it is heated to a point at which the substance glows.[9]

Other reactions, such as the production of aluminium and aluminium alloys, etc., in which aluminium nitride is formed incidentally to the main reactions are reported.[11–23]

The conversion of aluminium sulphide, Al_2S_3, into the nitride when heated in a current of nitrogen begins at 1430° and reaches 39% at 1750° after 2 hours. Bunet has reviewed (1935) some of the methods of production of aluminium nitride.[24]

PROPERTIES

Aluminium nitride becomes phosphorescent when activated by a small quantity of silicon. Two methods of preparation of the phosphor have been described:

(*a*) finely divided aluminium to which has been added pure silicon (or aluminium which contains up to about 10% SiO_2) is heated at 1300° in a molybdenum-lined nickel tube while a stream of ammonia is passed over it;

(*b*) aluminium chloride is purified by sublimation and converted by the action of ammonia into the additive compound $AlCl_3,NH_3$ which is vaporized at 400°C., and then mixed with nitrogen (previously bubbled through $SiCl_4$ to provide the necessary silicon) and then passed over a tungsten spiral heated to about 1000°C.[25] The AlN thus obtained is yellowish white, hard and shows pronounced phosphorescence. The activating effect commences with a silicon content of about 0·5%, is maximal at about 5% of silicon and then slowly decreases with increasing silicon content. Analysis of the spectral emission shows it to consist of very short wavelength radiation (under 300 $\mu\mu$), lying chiefly in the blue zone, and three bands analogous to those of boron nitride. The phosphorescence is best excited by the iron arc. Apparently no element other than silicon can activate aluminium nitride. *X*-Ray analysis of the AlN phosphor has crystalline structure of the diamond type, similar to that of silicon, and only with this structure is the material phosphorescent.[24] A red burning luminophore made of aluminium nitride activated with manganese has been reported.[26]

Neuman *et al.*[27] obtained $\Delta H = -57{\cdot}4$ kcal./mole for the heat of formation of AlN, whilst Satô [28, 29] gives a value of $-74{\cdot}7$ kcal./mole, and Prescott and Hincke[30] give $-80{\cdot}43$ kcal./mole. In a review, Kelley[31] gives Neumann's figure as the best value, but in a later paper Roth[32] prefers a value of 64 kcal./mole.

The free energy of formation is calculated to be $\Delta F^\circ_{298\cdot 1} = -72{\cdot}790$ kcal./mole[31] and a value of $\log K_p = 1{\cdot}46$ for the synthesis of the nitride, where K is the equilibrium constant for the reaction $Al(l) + \tfrac{1}{2}N_2 = AlN$, has been reported.[33]

The specific heat varies with temperature according to the equation:

$$C = 0{\cdot}1803 + 2{\cdot}750 \times 10^{-3}t - 1{\cdot}937 \times 10^{-7}t^2$$

When acetylene, alone or mixed with hydrogen or other gas, is passed at 700° over aluminium carbide, alone or mixed with carbon or aluminium nitride, aromatic hydrocarbons such as C_6H_6, $C_{10}H_8$, and Ph_2 are produced.[34] Finely divided aluminium nitride (less than 1 μ in diameter) can be used as a secondary accelerator in the vulcanization of butadiene–styrene rubbery copolymer.[35]

Nitrides of Gallium, Indium and Thallium

Gallium nitride, GaN, has been prepared as a dark-grey powder by the reaction between ammonia gas and metallic gallium at about 900°C. for several hours.[37–39] Attempts to prepare the nitride by the direct action of nitrogen on the metal were unsuccessful. The nitride can be obtained also by heating $(NH_4)_3GaF_6$ in ammonia at 900°C.[39]; thus produced it is a bright grey or yellow substance. It is an extremely stable compound which sublimes above 800°C. without decomposition. It is not reduced by hydrogen at 800°C. but it does react slowly with oxygen at this temperature to form gallic oxide. The nitride is unchanged when treated with a dilute or concentrated solution of hydrochloric, hydrofluoric or nitric acid. Hot aqua regia is without effect on the nitride, but it dissolves slowly in hot concentrated sulphuric acid and hot concentrated sodium hydroxide solution.[37–40]

A form of gallium nitride has been prepared also by streaming nitrogen activated by an electric discharge (produced at 2 mm. Hg) over liquid gallium. In this nitride gallium has a lower valency than in the normal compound, GaN, and this nitride can be decomposed by water, dilute acids and bases.

GaN has a hexagonal structure of the wurtzite type [38–40]with $a = 3{\cdot}160 \pm 0{\cdot}008$ A., $c = 5{\cdot}125 \pm 0{\cdot}010$ A., $c/a = 1{\cdot}622$ according to Lirman and Zhdanov,[38] and $a = 3{\cdot}18$ A., $c = 5{\cdot}16$ A., $c/a = 1{\cdot}625$ according to Juza and Hahn.[39, 40]

The heat of formation is $24{\cdot}9 \pm 0{\cdot}9$ kcal./mole and the magnetic susceptibility is $-0{\cdot}33_2$.

Indium nitride, InN, is obtained by heating $(NH_4)_3IF_6$ in a stream of ammonia at 600°C.[39] Cathodic volatilization of indium in nitrogen at low pressure is also said to yield InN.[42, 43] InN has the wurtzite structure, with $a = 3{\cdot}53_7$ A., $c = 5{\cdot}70$ A., $c/a = 1{\cdot}611$. The heat of formation is $4{\cdot}6 \pm 0{\cdot}5$ kcal./mole; the pycnometric density is 6·89 g./c.c., and the magnetic susceptibility is $-0{\cdot}32_2$.

Attempts to prepare thallous nitride by the reaction of ammonia with TlF,HF, thallous nitrite, thallous oxide or thallium gave at most 0·5% of the nitride.[39]

Nitrides of Rare-earth Metals

The heat of formation of scandium nitride is 75·0 kcal./mole.[44]

Lanthanum nitride, LaN, can be prepared[45] by passing nitrogen or ammonia over lanthanum heated to temperatures of 600–900°C. for periods ranging from 12 to 18 hours. It is also prepared by direct union of lanthanum and nitrogen[46] (see also cerium, below).

The crystal structure of lanthanum nitride is of the rock salt type with $a = 5{\cdot}275$ A.,[47] 5·29 A.,[45] $5{\cdot}295 \pm 0{\cdot}004$ A. The dissociation pressure of lanthanum nitride is very small at 900°C. On heating for 5 hours at 900° in high vacuum (5×10^{-5} mm. Hg), no loss in weight was detected. No evidence of superconductivity was obtained down to a temperature of 1·8°K.[46]

The heat of formation of the nitride is 71·055 kcal./mole.[27] The entropy and free energy of formation are estimated to be $\Delta S_{298 \cdot 1} = -25{\cdot}0$ e.u. and $\Delta F^\circ_{298 \cdot 1} = -64{\cdot}650$ kcal./mole.

Cerium nitride, CeN, is prepared by heating the metal in nitrogen.[47]

Perret and Banderet[48] have investigated the reaction of MCl_3 (M = Ce, La, Nd) when heated with sodium cyanide, in the presence of iron as a catalyst, at temperatures above 300°. The reactions occurring are:

$$MCl_3 + 3NaCN \rightarrow M(CN)_3 + 3NaCl$$
$$2M(CN)_3 \rightarrow M_2(NCN)_3 + 3C$$
$$M_2(NCN)_3 \rightarrow 2MN + 3C + 2N_2$$

Cerium nitride has the NaCl type structure with $a = 5{\cdot}01$ A.[47] No evidence for superconductivity was obtained down to a temperature of 1·8°K.[50]

The heat, entropy, and free energy of formation are $\Delta H = -78$ kcal./mole,[49] $\Delta S_{298 \cdot 1} = -25{\cdot}0$ e.u.[31] and $\Delta F_{298 \cdot 1} = -70{\cdot}550$ kcal./mole.[31]

Praseodymium nitride, PrN, is prepared by heating the metal in nitrogen.[47] It has the NaCl type structure with $a = 5{\cdot}15_5$ A.[47]

Neodymium nitride, NdN, is also prepared by direct reaction between the metal and nitrogen; the reaction is vigorous[1] (see also cerium nitride—above). It has the NaCl structure with $a = 5{\cdot}14$ A. The nitride decomposes readily in moist air with evolution of ammonia.[51]

A preparation of tempered gadolinium gave an *X*-ray pattern that could be explained on the basis of the formation of a surface layer of GdN. The nitride was verified through the atomic radius of the nitride ion, the intensities of the *X*-ray lines, and the molecular volume. It has the NaCl type structure with $a = 4{\cdot}99$ A.[1]

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NITRIDES OF GROUP IV METALS

Nitrides of Germanium

Germanic nitride, Ge_3N_4, can be prepared by heating germanium in ammonia at 650–700°C. It is a light-brown powder which is reduced by hydrogen at 700°C.; it reacts with oxygen at 850°C. and with chlorine at 600–700°C., and decomposes at 900–1000°C.[1] The same nitride may also be prepared by treating germanium tetrachloride with liquid ammonia and heating the resultant tetrammine to 350°C.[2]

For the reaction

$$3Ge + 4NH_3 \rightarrow Ge_3N_4 + 6H_2$$

the equilibrium data are as follow[3]:

$1/T \times 10^3$	1·133	1·128	1·097	1·079	1·067
K	$1{\cdot}52 \times 10^{-6}$	$2{\cdot}82 \times 10^{-6}$	$3{\cdot}37 \times 10^{-5}$	$9{\cdot}97 \times 10^{-5}$	$2{\cdot}60 \times 10^{-4}$

where $K = f^6_{H_2}/f^4_{NH_3}$.

Values of the dissociation constant for the reaction $Ge_3N_4 \rightarrow 3Ge + 2N_2$ are as follow:

T°K.	883	887	911	927	937
$K \times 10^{-6}$	19·63	12·10	2·224	1·250	0·6501.[3]

The heat of formation of Ge_3N_4 is $-15{\cdot}6$ kcal./mole.[4]

According to Juza and Hahn[4, 5] germanic nitride, Ge_3N_4, has a rhombohedral structure with $a = 8{\cdot}565$ and $\alpha = 107°46'$. Leslie *et al.*[6] (who prepared Ge_3N_4 by nitriding germanium with ammonia at 1300°F.) dispute this; because it was not possible to obtain the diffraction pattern for a single crystal, they were unable to determine the structure unequivocally. They considered, however, that the structure was orthorhombic with $a = 13{\cdot}84$ A., $b = 4{\cdot}06$ A., $c = 8{\cdot}18$ A., the substance being isomorphous with Si_3N_4 prepared from nitrided steels.

The magnetic susceptibility of germanic nitride was determined by the method of Pacault[7]; the experimental molal susceptibility is 90·6 as compared with a calculated value of 22·9 based on the law of additivity.

Germanous nitride cannot be prepared by the thermal decomposition of Ge_3N_4 or by combination of germanium and nitrogen.[8] It can be prepared, however, by heating the amide, $Ge(NH)_2$, at 250–300°C. This nitride is a dark brown substance which is readily hydrolysed by moisture or alkalis. Above 500°C., it dissociates into its elements.

Nitrides of Tin and Lead

The product of the reaction between stannic chloride and ammonia, viz., $2SnCl(NH_2)_3,NH_4Cl$, on heating to 100°C. and then washing with ammonia, yields the compound $Sn(NH_2)_3Cl$. When this is heated to 270° in vacuo SnNCl is formed and on further heating decomposition to Sn_3N_4 and $SnCl_4$ occurs.[9]

Cathodic volatilization of tin in a low pressure atmosphere is reported to give Sn_3N_4 as an iridescent black coating on the tube.[10] This compound does not react with water but with hydrogen chloride it forms stannic chloride and ammonium chloride.

A nitride of the composition Sn_3N_2 has been reported.[11]

Cathodic sputtering of lead in nitrogen at reduced pressure is reported[12] to give an easily pulverizable deposit. This reacts with water to give ammonia and litharge and is probably the nitride Pb_3N_2. The addition product of ammonia and lead tetrachloride, viz., $2PbCl(NH_2)_3,NH_4Cl$, on heating to 100° and washing with ammonia, forms the compound PbNCl, which on further washing polymerizes to $(PbNCl)_6$.[9]

Titanium Nitride

PREPARATION

Titanium nitride, TiN, can be prepared directly by combination of the metal and nitrogen.[13–15] Some workers use ammonia instead of nitrogen.[23] Agte and Moers[14] heated the pure metal for 1–2 hours at 1100–1200°C. in nitrogen. The nitride thus prepared was finely powdered and pressed into slugs at 2000 kg./sq. cm.: the slugs were then heated two to four times for about 15 minutes at 2300°C.; after each heating the slugs were ground and pressed. Finally the slugs were heated by direct current almost to the melting point in order to remove all impurities. Chiotti[13] was able to prepare the nitride by passing nitrogen (or ammonia) over metal shavings at 400–940°C. In the method used by Schomate and Naylor 99·5% pure TiN is obtained by heating titanium metal in a stream of purified nitrogen and hydrogen at 1400°C.[16, 17]

The reaction of titanium hydride with pure dry nitrogen at 1870°C. gives TiN.[18] It may also be prepared by heating the hydride in ammonia at 1000°C. for about 100 hours.[19]

Titanium oxide is also used as the starting point in some preparations, the oxide mixed with carbon being heated in nitrogen.[20, 21] Alternatively the oxide can be mixed with a slight excess of calcium hydride and then heated in ammonia or nitrogen[22]; the calcium oxide formed in the reaction prevents the titanium nitride particles from fusing together.

Titanium carbide also reacts with nitrogen to give the nitride. A feature of the reaction involved in the nitriding of TiC at 1300–1800°C. in a vacuum furnace is the formation of TiC–TiN solid solutions. The extent to which the carbide is nitrided at a given pressure diminishes as the temperature is raised. At temperatures above 1500°C., pressures in excess of 1 atm. must be used to effect complete nitriding.[24]

Finely divided titanium nitride is produced by the reaction of titanium sulphide with anhydrous ammonia at 900°C.[25]

If anhydrous ammonia is introduced into a molten mixture of a titanium halide and the halide of an alkali or alkaline earth metal, the titanium halide is reduced to form a finely divided precipitate of titanium nitride.[25]

Breger[26, 27] prepared the nitride by the reaction of titanium tetrachloride with ammonia at temperatures between 400° and 1500°C.; alternatively the compound $TiCl_4,nNH_3$ can be heated. During the preparation of titanium nitride by this method α and β $TiCl_4,4NH_3$ were obtained as intermediate products.[27, 34]

Titanium nitride in a very pure state can be obtained by deposition on a heated tungsten or tantalum filament from the vapour phase mixture of the tetrachloride with nitrogen and hydrogen.[28–31] Pollard and Woodward[30, 31] found in the continuous flow method that the critical filament temperature is 1250–1450°C., for $1:1N_2$–H_2 mixtures at 30–40 cm. pressure.

A surface film of titanium nitride can be deposited on iron by passing $TiCl_4$ vapour and nitrogen (with or without hydrogen) over the metal at 1200°C.[32, 33]

When purified titanium tetrachloride is vaporized in a current of purified nitrogen and passed through the silent electric discharge in an apparatus of the Becker and Fromandi type at 4500 v. the compound $TiNClTiCl_4$ is amongst the reaction products.[35]

The results of observations of cataphoresis, *p*H, conductivity titration and viscosity indicate that stable suspensions of titanium nitride can be formed only in an acid medium.[36] The stability of these suspensions is due to adsorption of hydrogen ions on the surface of the particles. Titanium nitride hydrolyses slowly when in the form of a fine powder suspended in water, ammonium hydroxide being formed. Suspensions in an acid medium are sufficiently stable for samples and crucibles to be formed by casting the suspension in plaster moulds, and after drying and firing at about 2000°C., a strong dense form of titanium nitride is obtained.

Titanium tetrachloride and cyanogen bromide combine easily to form $3TiCl_4$, 2BrCN; if this is vaporized at 80–90°C. in the presence of ammonia, titanium nitride is formed.[37]

Crystalline titanium nitride is obtained by melting the powder in an electric arc; it scratches glass and quartz, has high mechanical properties and is resistant to sudden temperature changes.[38]

The Titanium–Nitrogen System

The phase diagram of the titanium–nitrogen system (Fig. 3) has been delineated from microstructure, *X*-ray diffraction and melting point data by Palty, Margolin and Nielsen.[39] Prior to this, Nielsen[40] had constructed a preliminary diagram based on theoretical considerations and published data. In the preparation of the titanium–nitrogen alloys Palty *et al.* used titanium prepared by two different methods which give the so-called sponge titanium and iodide titanium. Slight differences were obtained in some cases and a detail from the phase diagram (Fig. 3), enlarged in Fig. 4, shows these discrepancies. The authors point out that the solubility of nitrogen in β-titanium appears to be lower for sponge titanium alloys probably because of the nitrogen present in the sponge as an impurity. No chemical analyses were made of the sponge titanium alloys and the total nitrogen content is in fact higher than the nominal composition. Furthermore the α transition for sponge titanium alloys occurs at lower temperatures than for iodide titanium alloys with equivalent (or higher) nitrogen content, apparently because of stabilizing impurities in the sponge, e.g. iron. However, this effect can also be attributed to an oxygen impurity.

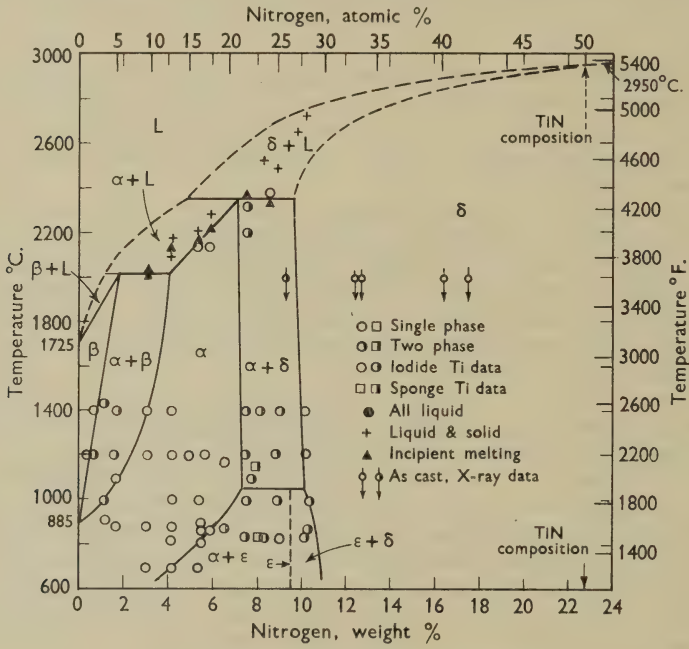

FIG. 3.—Titanium–nitrogen phase diagram

The lattice parameters found by Palty *et al.*[39] for α phase alloys are presented in Fig. 5; Clark's data[41] for 0% nitrogen are also included.

Palty *et al.*[39] state that some contamination occurred during the processing of the powdered specimens, and the result of this is evident in the lattice parameters; for the alloy with the lower nitrogen content they found that the *c* parameter exceeds Clark's value for a similar composition by about 0·04 A., whilst at higher nitrogen

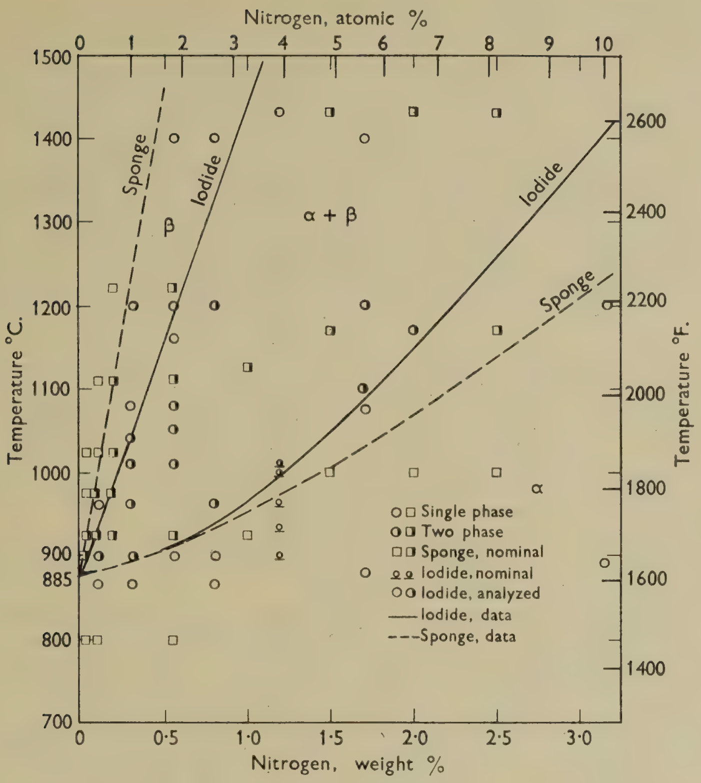

FIG. 4.—Titanium–nitrogen phase diagram

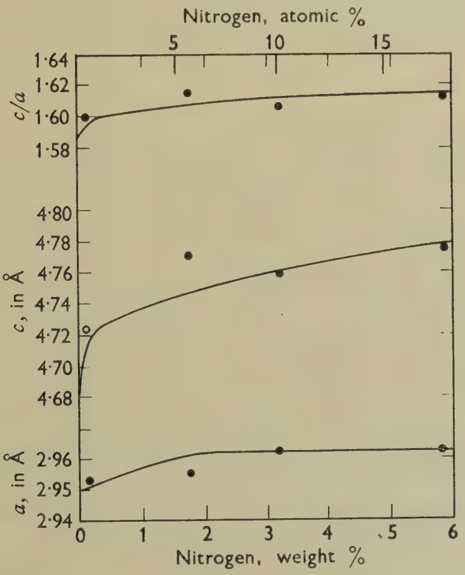

FIG. 5.—Lattice parameters of the alpha phase in titanium–nitrogen alloys

contents the trend of the data agrees with Ehrlich.[15] McQuillen[42] points out that the experimental scatter of the results obtained by Palty *et al.* is such that one cannot decide which values are correct; moreover, the continued upward trend of the c parameter in the range of 10–16 atom-% of nitrogen may or may not be a real effect. (Further references to the solubility of nitrogen in titanium are given below in relation to the kinetics of the reaction between these two elements.)

The δ (or TiN) phase has a wide range of homogeneity and possesses a cubic structure of the NaCl type. The lattice parameter of 'TiN', as prepared from $TiCl_4,nNH_3$ by heating, or from $TiCl_4+NH_3$ in the gas phase, varies from 4·21 to 4·235 A. between 400° and 1500° and is then constant[26, 27, 43, 44]; the range is the same for both methods of preparation. Below 1400°C. many of the titanium sites in the lattices are unfilled, but they gradually fill on heating; above 1600° the lattice is complete and is not subject to further change up to 3000°C. The density increases from 4·5 at 400° to 4·85 at 1000° and 5·1 at 1600°C. and then remains constant. On melting at about 3000° partial dissociation occurs and the two-phase system TiN and Ti is obtained. According to Ehrlich[15] the titanium nitride phase extends to the composition equivalent to $TiN_{0\cdot 42}$; the upper limit was not definitely fixed. Other values[45–47] reported for the lattice parameter of TiN range from 4·40 to 4·23 (KX): McQuillan[42] considers that the most probable value is 4·243 ± 0·002 A.

The ϵ phase[39] has a tetragonal unit cell with dimensions $a=4{\cdot}92$ A., $c=5{\cdot}61$ A., $c/a=1{\cdot}05$; the crystal structure has so far not been determined.

A further discussion of the phase relationship of the titanium nitride system has been given by McPherson and Hansen.[48]

It is well established that nitrogen has an extremely high solubility in titanium. In contrast to hydrogen, which is also extremely soluble,[49] the nitrogen taken up cannot be removed by heating in a high vacuum. However, in a more recent paper[50] it is reported that titanium nitride undergoes a second order decomposition in a vacuum at temperatures between 1000° and 1400°C.; below 1000°C. the evolution of gas is extremely slow. In this investigation it was found that hydrogen (adsorbed in the crystals of titanium nitride during preparation of the nitride by the reduction method) as well as nitrogen was evolved. Since the titanium atoms of titanium nitride are arranged in a face-centred lattice with nitrogen atoms placed interstitially in octahedral holes, hydrogen atoms could be accommodated in the tetrahedral holes of this lattice from which they would presumably diffuse to the surface as atoms, which then recombine and are desorbed as molecular hydrogen.

TITANIUM–NITROGEN REACTION RATE

The rate of the reaction between titanium and nitrogen is reported[51–53] to follow the parabolic law. By measuring the fall of pressure as a function of time at temperatures of 700°C. and 1000°C., the initial pressure being about 4/5 atmosphere, the rate of reaction was found to be not sensitive to nitrogen pressure.[51] These experiments were made with the specific object of elucidating the effect of titanium when heated in the ordinary atmosphere, similar experiments being conducted with oxygen at 1/5 atmospheric pressure. By computing the rate of bombardment of the surfaces and comparing the results with the initial measured rate of reaction, the probability that a collision between a gas molecule and a titanium surface will result in reaction, under the conditions of temperature and pressure prevailing in the experiments, was calculated to be 10^{-8} for nitrogen at 1000°C. which is considerably smaller than the value of 10^{-6} for oxygen at the same temperature; in other words, the rate of reaction for nitrogen is considerably less than for oxygen.

Gulbransen and Andrew[53] studied the absorption of nitrogen over the temperature range 500–850°C. at a constant pressure of one atmosphere.

Richardson and Grant[52] studied the reaction rate in a modified Sieverts type of apparatus by measuring the decrease in gas pressure at constant volume. A temperature range of 787–1014°C. and starting pressures of 0·2 to 0·5 atm. were used.

The isothermals of pressure versus time (see Fig. 6) show discontinuities; it is believed that the higher initial rates are caused by small amounts of oxygen contamination. The rate of reaction calculated from the section of the isothermal supposedly produced by pure nitrogen was found to be about one-fiftieth of that of the corresponding reaction with oxygen.

Wasilewski and Kehl[54] studied the absorption process (in a modified Sieverts apparatus) over the temperature range 800–1400°C. The rates throughout this range were in accordance with the parabolic law, and the deviations from the ideal law occurred during the initial reaction period, presumably because of rupture of the surface layer in course of formation, with consequent exposure of the metal beneath.

The energy of activation of adsorption is variously reported as 36·3 kcal./mole (below 800°C.),[53] 45·4 kcal./mole (above 800°C.),[52] 53·8 kcal./mole (at 1400°C.).[54]

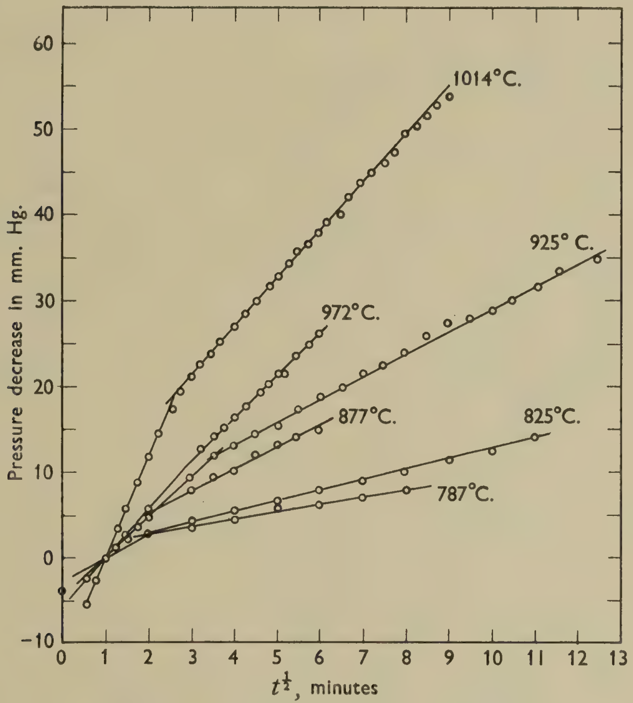

FIG. 6.—Reaction of nitrogen with titanium

Wasilewski and Kehl found that a reduction in nitrogen pressure causes a slight increase in the absorption rate, but no quantitative relationship between the pressure and reaction rate was established.

Carpenter and Reavell[51] observed that whilst in the reaction between oxygen and titanium a film of oxide forms which flakes off, in the corresponding nitrogen reaction the nitride film does not flake off.

Wasilewski and Kehl further observed that except for the specimens produced at or below 850°C. a golden-coloured film of titanium nitride was visible after reaction. Nitride layers were also formed at 850°C. and 800°C.; this nitride layer was adherent, very hard and brittle, and no detectable decomposition of the nitride took place in vacuo at temperatures up to 1400°C. At temperatures above 950°C. two surface layers were observed; these were identified as the nitride (thin outer layer) and the α phase (inner layer) surrounding a core which remained in the β condition. At

950°C., however, another layer was observed apparently subdividing the α layer: this was probably the ϵ phase. McQuillan[42] correctly points out that despite the fact that only a slight tarnish due to a surface film of titanium nitride appears below 1000°C., this does not mean that the metal has not adsorbed large amounts of nitrogen into solid solution.

Wasilewski and Kehl[54] have also studied the rates of diffusion of nitrogen through α and β titanium and also through titanium nitride; their results, expressed in graphs showing the variation of the diffusion coefficients with temperature, are given in Figs. 7 and 8. The diffusion coefficient can be expressed by the equations:

$$D_\alpha = 1{\cdot}2 \times 10^{-2} \exp \{(-45{,}250 \pm 2250)/RT\} \text{ cm.}^2\text{/sec.}$$
$$D_\beta = 3{\cdot}5 \times 10^{-2} \exp \{(-33{,}800 \pm 1400)/RT\} \text{ cm.}^2\text{/sec.}$$
$$D_{\mathrm{TiN}} = 5{\cdot}4 \times 10^{-3} \exp (-52{,}000 \pm 3500)/(RT) \text{ cm.}^2\text{/sec.}$$

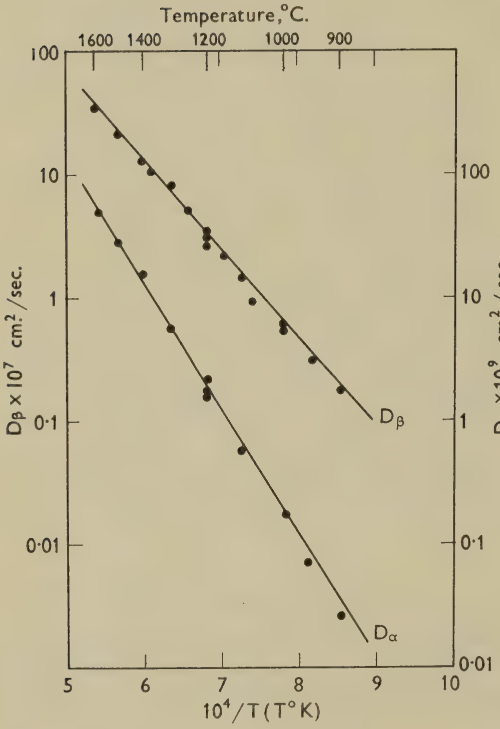

FIG. 7.—Variation with temperature of the diffusion coefficients of nitrogen and α- and β-titanium above the transformation temperature

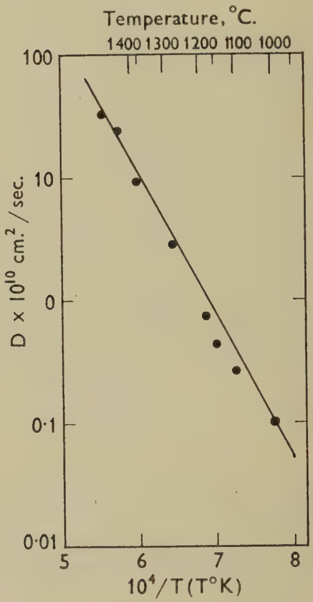

FIG. 8.—Variation with temperature of the diffusion coefficients of nitrogen in titanium nitride

From these data it seems that while the long-term reactions of titanium and nitrogen are controlled by diffusion through the titanium and nitride surface layer, the initial controlling reaction is more likely to be diffusion through the α structure. These authors consider that nitrogen may well be present in the interstices as negatively charged ions, as indicated by the enormous increase in hardness of titanium metal. They think it probable that the nitrogen diffuses in atomic form; for diffusion of ions it would be expected that the activation energies would be higher than those actually observed.

However, the data available so far do not permit a determination of the state of the nitrogen atom when in an α- or β-titanium lattice. The metallic characteristics of the nitride (similarly the monoxide) of titanium indicate that this structure is not ionic.

THE TITANIUM–CARBON–NITROGEN SYSTEM

Some aspects of the Ti–C–N system have been investigated.[46, 55–57]

Stone and Margolin[57] investigated the titanium-rich region of the Ti–C–N system in the temperature range 500–1400°C. and in the composition range up to 2% of carbon and 5% of nitrogen.[42] Isothermal sections for 800°, 900°, 1000° and 1300°C. are shown in Figs. 9 to 12. It was established that:

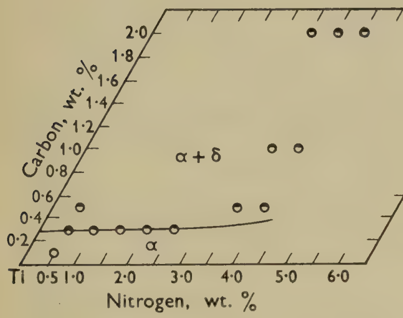

FIG. 9.—Isothermal section at 800°C. in the Ti–C–N system

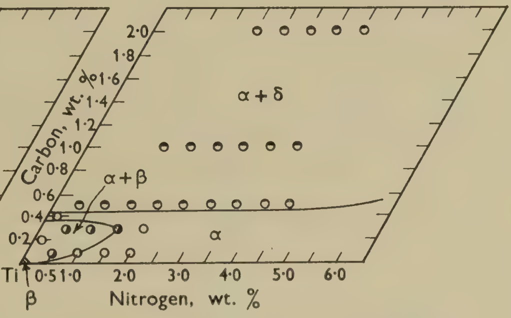

FIG. 10.—Isothermal section at 900°C. in the Ti–C–N system

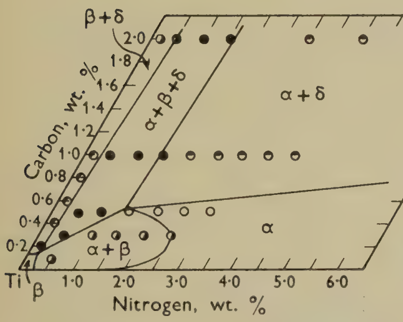

FIG. 11.—Isothermal section at 1000°C. in the Ti–C–N system

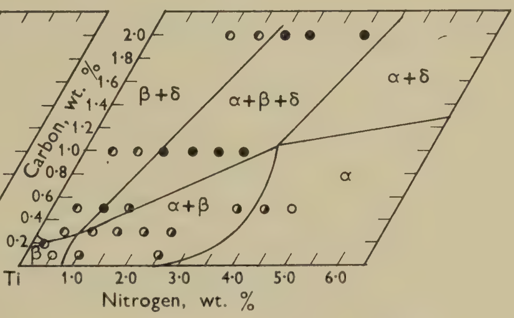

FIG. 12.—Isothermal section at 1300°C. in the Ti–C–N system

(1) the addition of nitrogen to alloys containing 2% of carbon results in a rise in the liquidus temperature from 1935°C. at 0% of nitrogen to approximately 2510°C. at 3·5% of nitrogen, and a rise in the temperature of the solidus surface to approximately 2070°C. at 2·5% of nitrogen;

(2) The addition of from 1–2·5% of nitrogen to alloys containing 0·5% of carbon has little effect on the incipient melting temperature which is approximately 1735°C. Beyond this point the solidus temperature rises with increasing nitrogen content.

X-Ray examination of the so-called titanium cyanonitride[77–79] with 71·5% of titanium, 2·6% of vanadium, 17·6% of nitrogen and 3·3% of carbon showed the presence of a sodium chloride structure with a mean value of $a = 4{\cdot}242$ A.; this consists primarily of a solid solution of TiC and TiN in the ratio 1:4·7 in which vanadium may replace titanium.

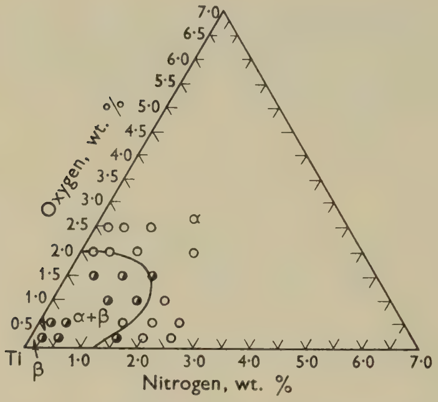

FIG. 13.—Isothermal section at 1000°C. in the Ti–N–O system

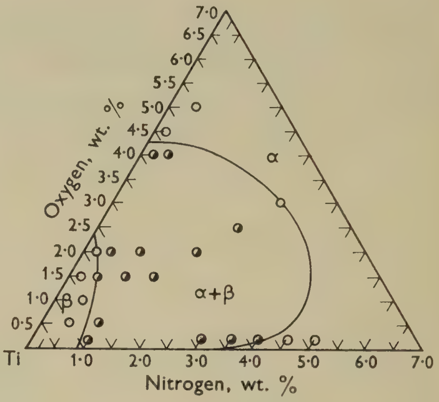

FIG. 14.—Isothermal section at 1400°C. in the Ti–N–O system

The Ti–N–O system has similarly been studied[55, 57] for the temperature range from 1000–1400°C. with alloys containing up to 6% of total alloying content; characteristic isothermal sections for 1000°C. and 1400°C. are shown in Figs. 13 and 14.[57] The phase diagrams of the titanium-rich portion of the ternary system Ti–Al–N from 0–10 wt.-% of aluminium and up to 0–1 wt.-% of nitrogen have been determined.[58]

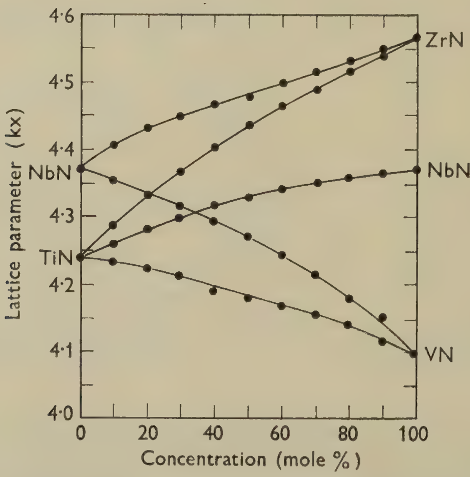

FIG. 15.—Lattice parameter vs. composition curves for nitride pairs

The phase relationships in the binary systems of various carbides and nitrides of titanium, zirconium, niobium and vanadium have been established, and the lattice parameters versus composition curves for these systems are shown in Figs. 15–18.[18]

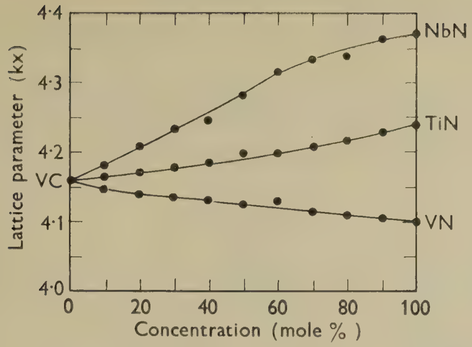

FIG. 16.—Lattice parameter vs. composition curves for vanadium carbide-nitride systems

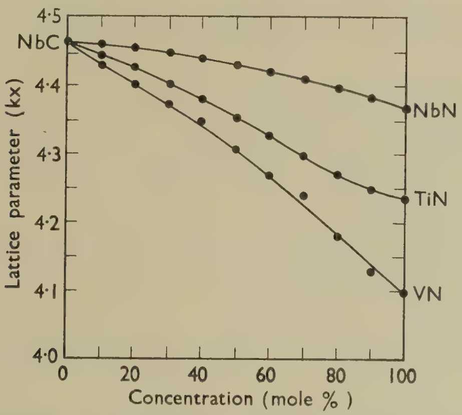

FIG. 17.—Lattice parameter vs. composition curves for niobium carbide-nitride systems

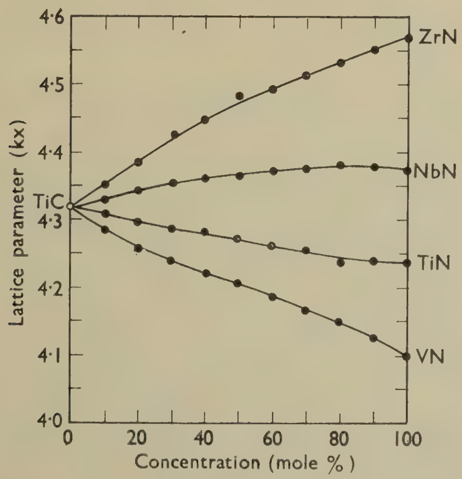

FIG. 18.—Lattice parameter vs. composition curves for titanium carbide-nitride systems

THERMODYNAMIC PROPERTIES OF TITANIUM NITRIDE

The heat content and specific heat (molar heat capacity) of titanium nitride in the temperature range 373–1735°K. are summarized in the following equations.[17]

$$H_T - H_{298{\cdot}16} = 11{\cdot}91T + 0{\cdot}00047T^2 + (296{,}000/T) - 4585$$
$$C_p = 11{\cdot}91 + 0{\cdot}00094T - (296{,}000/T^2)$$

Some values of the heat content and entropy are as follow:

T°K.	$H_T - H_{298{\cdot}16}$ kcal./mole	$S_T - S_{298{\cdot}16}$ e.u.
400	1,000	2·88
1,000	8,050	13·52
1,800	18,510	21·18

Values of the specific heat at low temperatures[16] are:

T°K.	52.5	104·6	155·6	206·0	298·16
C_p (g.-cal./mole)	0·527	2·781	4·977	6·705	8·86

From these figures the entropy is estimated to be 0·13 e.u. for the temperature range 0–52·00°K., and 7·07 e.u. for the range 52·0–298·6°K. and 7·20 ± 0·04 e.u. at 298·16°K.

The standard heat of formation calculated from combustion data is $-80{\cdot}4_7 \pm 0{\cdot}2_7$ kcal./mole.[59] This is in good agreement with Neumann's value of −80·3 kcal./mole.[60] The free energy of formation is calculated to be $-\Delta F^\circ = 73{\cdot}65 \pm 0{\cdot}27$ kcal./mole.

Bridgman has investigated the compressibility of titanium nitride.[58] Münster and Ruppert[33] have also reviewed (1953) some of the data on the thermodynamic properties of titanium nitride.

Titanium nitride is super-conducting. A transition temperature of 1·2°K. has been obtained[61–63] but more recent work gives the temperature as 5·6°K.[64, 65]

The specific resistance of titanium nitride at room temperature and liquid air temperature is $0{\cdot}217 \times 10^{-4}$ and $0{\cdot}0813 \times 10^{-4}$ ohms/cm. respectively.[66] Clausing[67] gives $0{\cdot}1107 \times 10^{-4}$ ohms/cm. at 0°C., and a temperature coefficient of $\alpha = 0{\cdot}00409$ per degree. Using another method, he also obtained a specific resistance of $0{\cdot}1152 \times 10^{-4}$ ohms/cm. and $\alpha = 0{\cdot}00489$ per degree. In addition Clausing observed an unusual hysteresis effect which he attributed to traces of metal in the nitride. Bridgman has reported the effect of pressure on the electrical resistance of titanium nitride.[68]

A magnetic susceptibility of $+0{\cdot}8 \times 10^{-4}$ for titanium nitride has been determined.[69]

DECARBURIZATION OF TITANIUM CARBIDE

A study has been made of the decarburization of titanium carbide by nitrogen and oxygen at temperatures ranging from 1200° to 1800°C. At 1200°C. in an atmosphere virtually of hydrogen (with small quantities of oxygen and nitrogen entering the furnace from the atmosphere) there is practically no nitridation and the oxidation increases with time until the oxygen content reaches approximately 25% after 9 hours. At 1400°C. oxidation diminishes with time and nitridation increases from 0·74% of nitrogen at 3 hours to 4% after 9 hours. At 1800°C. nitridation is still more intense and increases from 2·3% of nitrogen at 3 hours to 7% at 9 hours, while the oxygen content decreases from 2·7% to 0·88% during the same time. Experiments in an atmosphere of hydrogen with 10% of nitrogen or in nitrogen alone show similar results except that in nitrogen nitridation is more intense. It is assumed from this that at 1900–2000°C. the only decarburizing element is nitrogen.[70]

The effect of nitrogen on the sintering and properties of titanium–tungsten alloys has been studied using alloys containing 15% TiC, 79% WC and 6% Co. No nitrogen was evolved during sintering of mixtures containing from 0·3 to 1·64% of nitrogen. The presence of nitrogen in the titanium carbide did not hamper the compacting of the alloy, nor did it affect the mechanical properties of the product. Up to 13%

of nitrogen did not impair the cutting properties of the alloy. This tends to indicate that nitrogen remains dissolved in the carbide.[70]

OXIDATION OF TITANIUM IN AIR

An investigation has been made by Arkharov *et al.*[71] of the rôle played by nitrogen in the high temperature oxidation of titanium in air. In pure oxygen the rate of oxidation of titanium between 700° and 1200°C. increases with temperature (T) according to the equation:

$$\Delta G = A\mathrm{e}^{-(b/T)}$$

where ΔG = gain of weight in a definite time interval, and A and b are constants. In air titanium is oxidized less than in oxygen in the temperature range 700–1000°C., but from 840°C. upwards the rate of oxidation in air increases with the temperature faster than in oxygen; the curve of $\log \Delta G$ as a function of $1/T$ has a break at that temperature, draws increasingly closer to the curve in oxygen and intersects it about 1150°C. At still higher temperatures titanium oxidizes in air more easily than in pure oxygen. *X*-Ray examination shows that the scale formed by oxidation is always rutile titania with some monoxide in the thin inner layer close to the metal. In the scale formed by oxidation in air at 1100–1200°C., there is also some Ti_2O_3 in the middle layer. The rutile formed in air at 1100–1200°C. shows an increase in the lattice constant, a, by 0·003 Å. and a decrease in c by 0·002 Å. as compared with the rutile formed in pure oxygen. No such differences are found in the products of oxidation at lower temperatures. At the higher temperatures the difference between the lattice constants of the rutile formed in air and in oxygen increases with the depth of the layer. When the rutile formed by oxidation in oxygen or chemically pure rutile is annealed in nitrogen for 24 hours, its lattice constants change and approach those of the rutile produced by oxidation of titanium in air. Consequently on oxidation in air or on heating in nitrogen, some nitrogen atoms enter the rutile lattice, most probably in the form of N^{3-} ions which replace O^{2-} ions in the ratio of 2:3,

The effect of nitrogen on the mechanical and physical properties of α-titanium has been reported.[72–74]

An *X*-ray investigation of the meteoritic mineral osbornite showed this to have the same cubic face-centred lattice as titanium nitride.[75]

An interpretation of the metallic properties of titanium nitride in terms of electronic structure has been presented.[76] (The reader is referred also to the general introduction on this aspect, page 151.)

Some uses and metallurgical aspects of titanium nitride have been discussed.[80–92]

Zirconium Nitride

PREPARATION

Zirconium nitride can be prepared by heating zirconium in nitrogen at 1100–2000°C.[14, 28, 67, 93] The nitride is also prepared by the method of van Arkel, i.e. by the decomposition of zirconium tetrachloride vapour in the presence of nitrogen and hydrogen by contact with a hot tungsten filament at 2300–2800°C.[14] Foster[19] has prepared the nitride by heating zirconium hydride in a stream of ammonia at 1000°C. for about 100 hours.

Chiotti[13] prepared the nitride by passing nitrogen and ammonia for 12 to 23 hours over the metal heated to about 700°C., special precautions being taken to exclude air from the sample during handling and weighing.

The nitride can be prepared from zirconium oxide by first reducing this with magnesium to produce the metal, which is then treated with nitrogen or ammonia.[94] Alternatively zirconium carbide can be prepared as an intermediate by heating zirconium oxide, zinc chloride and charcoal; if hydrazine is added to this mixture zirconium nitride is obtained.[94]

Zirconium nitride and a sub-nitride were reported by earlier workers (see Mellor, VIII, 120), but most of the later work indicates the existence of only the yellow compound, ZrN.

According to Ishii[95, 96] there are two modifications of ZrN.

Clausing showed[67] that filaments of zirconium (containing less than 0·5% of hafnium) when heated electrically to 2000°K. absorb nitrogen, the change in weight corresponding to the formula ZrN. Using a similar method de Boer and Fast[97] found that zirconium can dissolve nitrogen up to a maximum of about 20 atom-%. Above this limit zirconium nitride is formed. The dissolved nitrogen increases the electrical resistance of zirconium and raises the α–β transition temperature of the metal just as oxygen does. Jaffee and Campbell[98] also report a similar solubility limit.

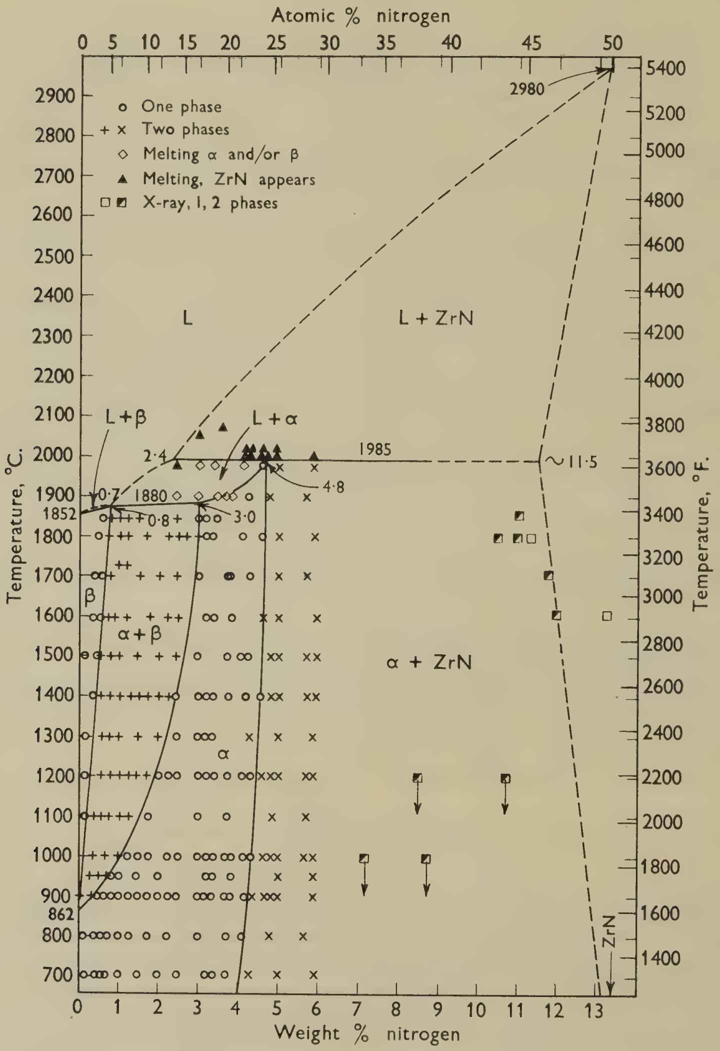

FIG. 19.—Partial diagram of the Zr–N system showing phase relationships up to ZrN

This solubility limit for nitrogen in the α phase is of the same order of magnitude (25 atom-%, i.e. 4·8 wt.-% at 1985°C.) as that found by Domagala *et al.*,[99] whose partial phase diagram, up to 50 atom-%, for the zirconium–nitrogen system is given in Fig. 19. It will be seen that α-zirconium has a maximum solubility for nitrogen of 4·8 wt.-%, i.e. 25 atom-% at 1985°C., which decreases to about 4·0 wt.-% (21 atom-%) of nitrogen at 600°C. At the temperature of the peritectic formation of β-zirconium 0·8 wt.-% (5·0 atom-%) of nitrogen is soluble in the β-phase. This solubility decreases to zero at the transition temperature. The intermediate-phase zirconium nitride has a range of homogeneity extending from about 11·5 wt.-% (46 atom-%) of nitrogen at 1985°C. to nearly stoicheiometric ZrN (13·3 wt.-%, 50 atom-%) at temperatures below 600°C. The highest average nitrogen content reached in the nitriding of various samples of zirconium powder at temperatures up to 1800°C. was about 11%; in other words no compounds with a nitrogen content other than that corresponding to ZrN could be prepared.

Guldner and Wooten[100] have reported that they were able to prepare a compound with 13 atom-% of nitrogen.

The kinetics of the reaction of nitrogen with zirconium have been studied by various workers in the following temperature ranges: 400–825°C.,[103] 862–1053°C.,[104] 900–1640°C.,[105, 106] and 700–1200°C.[107] Fig. 20 shows the absorption isotherms for α-zirconium at 7·6 cm. Hg pressure obtained by Gulbransen and Andrew,[103] who find that the reaction rate is much slower than for the corresponding reactions with oxygen and hydrogen. The nitride reaction is insensitive to pressure in the range studied, i.e. 7·6 to 0·15 cm. Hg, and does not follow any simple pressure function.

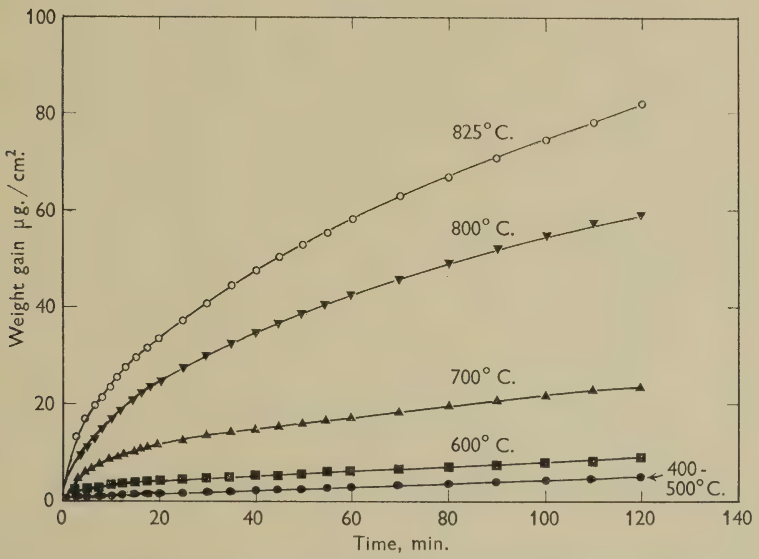

FIG. 20.—Effect of temperature on the reaction of zirconium with nitrogen at 7·6 cm. Hg pressure

All the above workers report that the reaction of nitrogen with either α- or β-zirconium follows a parabolic law. Energies of activation in kcal./mole for the reaction are: for α-zirconium 39·0[103] and for β-zirconium 52·0,[104] 67·5 with a high hafnium content, 2%, or 48·0 for a low hafnium content, 0·015%.[106]

Zirconium nitride has a cubic structure of the sodium chloride type. The lattice parameter is 4·57 to 4·59 A.,[13] 4·567 kX.[18] or 4·63 A.[101] Schönberg[102] found that the lattice parameter varies between 4·537 and 4·562 A., and thinks that the high value of $a = 4{\cdot}63$ A. reported by some workers is most probably due to the presence of oxygen in the lattice.

DIFFUSION OF NITROGEN IN ZIRCONIUM

Figure 21 gives the diffusion coefficient of nitrogen in β-zirconium with a low hafnium content, 0·015%, for the temperature interval 920–1640°C.[106]; zirconium with a high hafnium content (2%) shows slightly smaller diffusion coefficients. The data conform to the equations:

$$D_\beta = 1{\cdot}5 \times 10^{-2} \exp \frac{(-30{,}700)}{RT} \qquad \text{(for low Hf content)}$$

and

$$D_\beta = 3{\cdot}010^{-2} \exp \frac{(-33{,}600)}{RT} \qquad \text{(for high Hf content)}$$

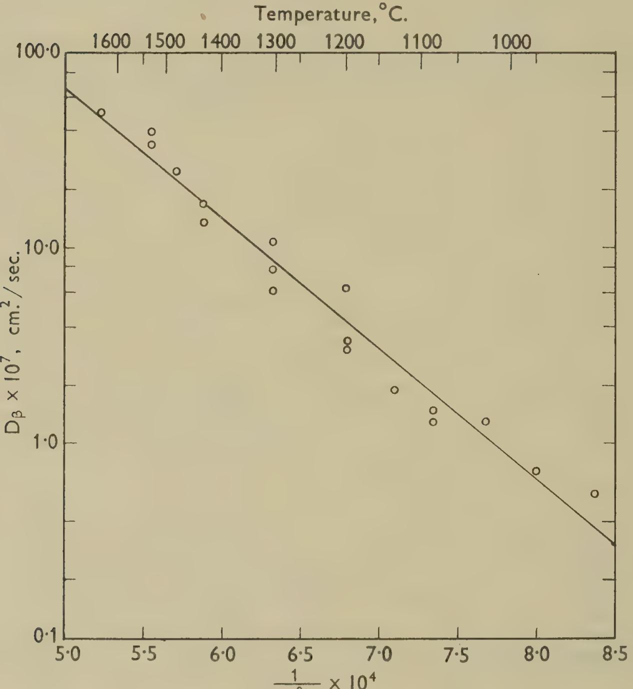

FIG. 21.—Diffusion of nitrogen in zirconium: variation of diffusion coefficient with temperature

The energies of activation for diffusion in the two types of zirconium are 30·7 and 33·6 kcal./mole respectively. The entropy of activation in the former case is 3·5 cal./mole degree. It is interesting to note that these diffusion activation energies are considerably lower than those for the reaction of gaseous nitrogen with zirconium; this seems to indicate that the rate of solution in the β-phase is not the rate controlling process.

From the diffusion data the limiting solubilities of nitrogen in β-zirconium were determined. Fig. 22 shows the solubility limit of nitrogen in β-zirconium with high and low hafnium contents.[106] The solubility limit is the concentration in grams inside the interface between the α- and β-phases. The heat of solution for nitrogen in zirconium is $\Delta H = 12{,}900 \pm 500$ g.-cal./mole.

Both nitrogen and oxygen are involved in the scaling of zirconium in air. A two-layered scale is formed with sufficient time, an outer white or buff scale (ZrO_2) and an inner black scale (ZrO_2, ZrN and possibly N). The white scale predominates below 1050°C. and the black above that temperature.[108] During processing zirconium may be contaminated by nitrogen, oxygen, carbon or hydrogen. At room temperature nitrogen, oxygen and carbon strengthen zirconium, but the strengthening is lost on heating to relatively low temperatures; consequently zirconium has good hot-working characteristics.[109]

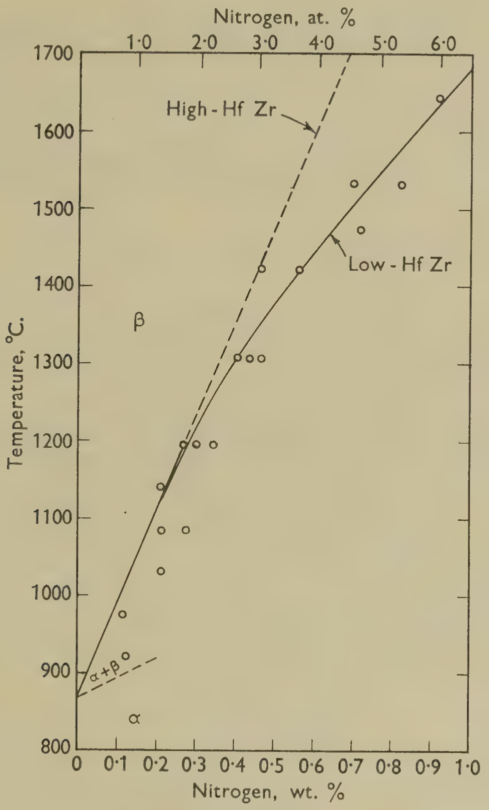

FIG. 22.—Solubility limits (C_0) of nitrogen in β-zirconium

THERMODYNAMIC PROPERTIES

The heat of formation is $\Delta H = -82{\cdot}200$ kcal./mole[60] and the specific heat in the temperature range 0–500°C. conforms to the equation:

$$C = 0{\cdot}9946 + 9{\cdot}242 \times 10^{-5}T - 9{\cdot}75 \times T^{2}$$ [110]

Smoothed values of the high temperature heat content and entropy of zirconium nitride over the temperature range 400–1700°K. are as follow[111]:

T°K.	400	600	800	1000	1,200	1,400	1,700
$H_T^\circ - H^\circ_{298\cdot16}$	1040	3260	5670	8190	10,760	13,370	17,360
$S_T^\circ - S^\circ_{298\cdot16}$	3·00	7·48	10·94	13·75	16·10	18·11	20·69

From these data the following specific heat equation has been deduced:

$$C_p = 11{\cdot}10 + 1{\cdot}68 \times 10^{-3}T - 1{\cdot}72 \times 10^{-5}T^{-2}$$

Low temperature values of the specific heat of zirconium nitride have been reported,[112] a selection of which is given below:

T°K.	53·1	77·6	114·9	155·9	206·7	246·0	298·16
C_p g.-cal./deg.	1·198	2·574	4·416	6·137	7·784	8·714	6·655

The entropy of zirconium nitride at 298·16°K. is $S^\circ_{298\cdot16} = 9\cdot29 \pm 0\cdot05$ e.u.[112] This value is virtually identical with the entropy of zirconium metal at 298·16°K.[111, 112]

The free energy of formation of the nitride as calculated from the preceding data is $\Delta F^\circ_{298\cdot16} = -75{,}400$ g.-cal./mole.[111, 112] This is in good agreement with Kelley's earlier value of $\Delta F^\circ_{298\cdot16} = -75{,}640$ g.-cal./mole.[113] The melting point is 2980 ± 50°C.[114] The magnetic susceptibility is $0\cdot6 \times 10^{-6}$.[97]

Agte and Moers[14] found that the specific electrical resistance of zirconium nitride is 0·136 and $0\cdot0397 \times 10^{-4}$ ohm cm. at room and liquid air temperatures respectively.

The transition temperature for super-conductivity is 9·05°K.[65]

Hafnium Nitride

Hafnium nitride can be prepared by methods similar to those used for the preparation of zirconium nitride. Campbell and co-workers[28] found that conditions for the vapour phase deposition from hafnium tetrachloride, nitrogen and hydrogen are almost the same as those for the corresponding zirconium compound.

Hafnium nitride, HfN, can be prepared by heating hafnium powder (97% pure, with zirconium as its major impurity) in a nitrogen atmosphere at 2000°C. It has, like zirconium nitride, a face-centred cubic structure with $a = 4\cdot52 \pm 0\cdot02$ A. The nitride has metallic character and is isomorphous with the carbide and monoboride of hafnium.[115] It has a melting point of 3310°C.[115] According to Satô[116] the heat of formation $\Delta H = -78\cdot3$ kcal./mole, but a more recent determination by Humphrey[117] gives a value of $\Delta H_{298\cdot16} = -88\cdot24$ kcal./mole. The entropy $S^\circ_{298\cdot16} = 13\cdot1$ e.u.; and the free energy of formation $\Delta F^\circ_{298\cdot16} = -81\cdot400 \pm 0\cdot5$ kcal./mole.[117]

Thorium Nitride

It has been observed that in the decomposition of a thorium halide by a glowing tungsten wire at about 2600°C. in nitrogen, small quantities of a black crystalline nitride having low electrical conductivity are formed;[118] this nitride is probably Th_3N_4.

By passing ammonia over thorium shavings at a temperature of about 750°C. for 12 hours Chiotti[13] obtained a nitride which corresponded closely to the composition Th_2N_3. Zachariasen[119] found that Th_2N_3 could also be prepared by the action of ammonia on thorium hydride at 1000°C. According to Chiotti Th_2N_3 has a hexagonal structure with lattice constants $a = 3\cdot87$ A., $c = 6\cdot16$ A. Zachariasen[119] confirmed this structure with $a = 3\cdot875 \pm 002$ kX., $c = 6\cdot175 \pm 0\cdot004$ kX.; the lattice is isostructural with La_2O_3 and contains 1 molecule in the unit cell. Th_2N_3 is unstable at high temperatures and if heated above 1500°C. decomposes with the formation of the mononitride, ThN.

The nitride prepared by the hydride–ammonia reaction[4] is stable at 1730°C. and has an equilibrium gas pressure of approximately 0·001 atm. at 2230°C., but it is readily hydrolysed by water or moist air; it is pointed out that there is insufficient evidence to prove if this is the nitride 'Th_3N_4'.

The interstitial nitride ThN has a face-centred cubic structure containing four molecules in the unit cell (NaCl type) with a lattice constant $a = 5\cdot2$ kX. This structure was predicted earlier by Rundle.[120] At high temperatures it appears to be unstable: its melting point determined under helium is about 2630°C.

Fox[121] has reported that the electron diffraction pattern of the reaction product of thorium with nitrogen indicates a new phase, believed to be a nitride, having a body-centred cubic structure with $a = 4\cdot55$ A.

Refs. p. 183

The rate of reaction of thorium with nitrogen for the temperature range 670–1490°C., at 1 atm. pressure, has been determined.[122] The reaction was found to follow a parabolic law; the parabolic rate law constant is given by

$$k = 5{\cdot}9\ \mathrm{e}^{-24,300/RT}\ \text{sq. cm./sec.}$$

The energy of activation of the reaction is 24,300 ± 1300 g.-cal./mole. The coefficient for the diffusion of nitrogen in thorium over the temperature range 845–1490°C. at 1 atm. is given by

$$D = 2{\cdot}1 \times 10^{-3} \times \mathrm{e}^{-22,500/RT}\ \text{sq. cm./sec.}$$

In the temperature range 700–1500°C. the solubility limits range from about 0·01% N_2 (by weight) to 0·033 wt.-% respectively.

The specific heat of Th_3N_4 over the temperature range 0–503°C. conforms to the equation[123]:

$$C_p = 0{\cdot}04895 + 4{\cdot}436 \times 10^{-5} \times t - 1{\cdot}384 \times 10^{-8} \times t^2$$

The heat of formation of Th_3N_4 is $\Delta H = -310{\cdot}4$ kcal./mole,[60] from which a free energy of formation of $\Delta F^{\circ}_{298{\cdot}1} = -52.17$ kcal./mole has been calculated.[113]

No evidence for super-conductivity was found down to a temperature of 1·2°K.[61–65]

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NITRIDES OF GROUP V METALS

Vanadium Nitrides

Pure vanadium nitride can be prepared from ammonium vanadate by the method of Epelbaum *et al.*[1–6] When ammonium vanadate is heated in ammonia at various temperatures the following products are formed: at 200–300°C. the product is 90% V_2O_5; at 300°C. 89% V_2O_5 and 6% V; at 400°C. 61% V_2O_4 and 12% VN; at 600°C. 70·1% V_2O_4, 9·9% V_2O_3, and 20% VN; at 700°C. 55% V_2O_3 and 41% VN; at 800°C. 53% VN and 44% V_2O_3; at 900°C. 92% VN and 8% VO; at 1100°C. 99% VN.

Hahn[2] following this procedure caused ammonium vanadate to react with ammonia at 900–1000°C. for several hours. Vanadium nitride can be prepared by

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nitriding 'pure' vanadium metal with nitrogen.[7] The lower nitride, the 'V_3N' phase of Hahn, was prepared by sintering vanadium nitride with vanadium metal in sealed quartz tubes at 1000–1100°C. for 24 hours.

Agte and Moers[8] deposited vanadium nitride from VCl_4–N_2–H_2 vapour mixtures on tungsten wires at temperatures from 1100° to 1600°C., whilst Pollard and Fowles[9] found an optimum deposition temperature at 1540–1570°C. and obtained a product consisting of yellowish-brown cubic crystals.

The V–N system has been investigated thoroughly by Hahn[2] and his work was confirmed in all respects by Schönberg.

The solid solubility of nitrogen in vanadium has been described as very small, but Rostoker and Yamamoto[11] found that the solubility is less than 3·5 atom-% at 900°C. but at least 3·5 atoms-% N at higher temperatures. Some work on the relation between hardness and lattice parameter confirms that nitrogen is to some extent soluble in vanadium and that there is a solubility range. The phase VN (γ phase) is well established. According to Hahn[2] it has a wide homogeneity range extending from $VN_{1\cdot00}$ to $VN_{0\cdot71}$, the upper limit representing the stoicheiometric nitride VN. According to Epelbaum and Ormont[3] the upper limit extends to $VN_{1\cdot04}$. Besides this phase only one other nitride phase exists which has a homogeneity range of $VN_{0\cdot37}$–$VN_{0\cdot43}$, this range including the stoicheiometric nitrides, V_3N and V_2N, previously reported (Mellor, VIII, 125). Hahn refers to it as the 'V_3N' phase. The nitride V_2N_2 reported in the earlier literature (Mellor, VIII, 125) does not exist.

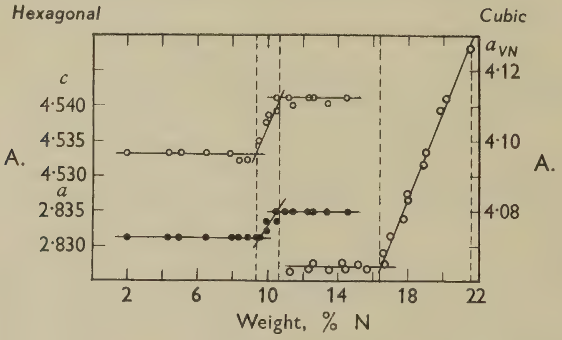

Fig. 23.—Lattice constants in the vanadium–nitrogen system

'VN' has a face-centred cubic structure with the lattice constant 'a' increasing from 4·064 A. ($VN_{0\cdot71}$) to 4·126 A. ($VN_{1\cdot00}$). The variation of 'a' with nitrogen content is shown in Fig. 23.[2] According to Epelbaum and Ormont[3] the lattice parameter decreases to 4·113 A. at 51.0 at.-% of nitrogen. These authors find also that specimens of vanadium nitride obtained either by heating ammonium vanadate or by partial oxidation of vanadium nitride and containing vanadium, oxygen and nitrogen are solid solutions of vanadium oxide in vanadium nitride; furthermore the lattice spacing is 4·08 A. for pure vanadium oxide and increases linearly with the concentration of vanadium nitride to 4·129 A. for pure vanadium nitride. For the stoicheiometric nitride VN the lattice parameter 'a' is 4·126 A. according to Hahn.[2] Other reported values are 4·169 A.,[10] 4·129 ± 0·001 A.[5] and 4·097 A.[83]

The $VN_{0\cdot37-0\cdot43}$ phase has a hexagonal lattice with lattice parameters: $a = 2{\cdot}835$ A.; $c = 4{\cdot}541$ A.; $c/a = 1{\cdot}602$ ($VN_{0\cdot37}$); and $a = 2{\cdot}831$ A.; $c = 4{\cdot}533$ A.; $c/a = 1{\cdot}602$ ($VN_{0\cdot43}$).[2] (See Fig. 23.)

The tetragonal nitride phase reported by Rostoker and Yamamoto[11] is thought to contain oxides of vanadium.

The VN phase has a metallic lustre and a bronze colour at the high nitrogen contents; with lower contents the colour is steel grey.[2] The 'V_3N' phase of Hahn is scarcely distinguishable from vanadium metal. The nitride, VN, is very stable in moist air at room temperature and also towards most acids. Only concentrated nitric acid appears to have any appreciable effect; concentrated sulphuric acid dissolves it only after prolonged boiling, nitrogen being evolved. Aqueous alkalis have little effect, but molten potassium hydroxide decomposes the nitride with evolution of ammonia. The 'V_3N' phase is chemically less stable than the VN phase. The densities of various vanadium nitride preparations as determined by a pycnometric method and *X*-ray analysis are as follow[2]:

Nitride	Density, g./c.c.	
	Pycnometric d_{25}	*X*-Ray
$VN_{1\cdot00}$	6·040	6·102
$VN_{0\cdot87}$	5·988	6·089
$VN_{0\cdot72}$	5·972	6·066
$VN_{0\cdot38}$	5·967	5·987

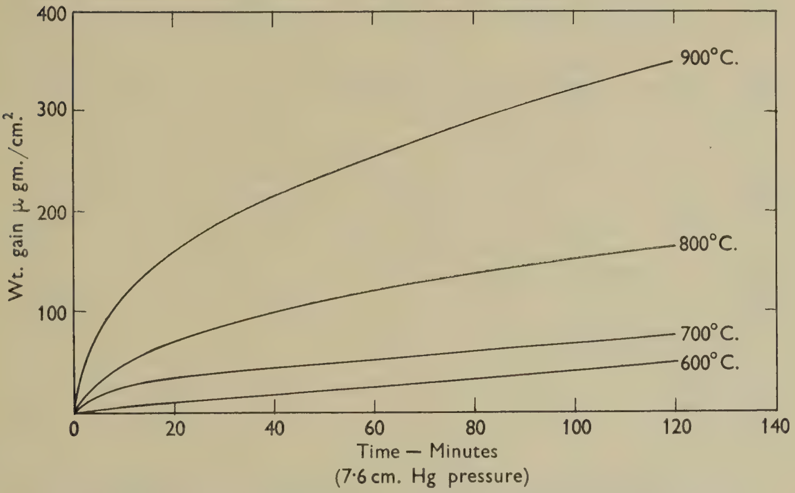

FIG. 24.—Effect of temperature on the reaction of nitrogen with vanadium

Anelastic effects in iron[20] and effects on strain ageing of mild steel[21] produced by presence of vanadium and nitrogen have been reported. Addition of vanadium nitride improves the tempering properties of steel,[22] the heat-resistance of molybdenum–silicon alloys[23] and Young's modulus of some aluminium alloys.[24]

The kinetics of the reaction of nitrogen with vanadium have been investigated over the temperature range 600–900°C. by Gulbransen and Andrew.[25] The rate of reaction is much less at a given temperature than for the corresponding oxidation. It is similar in magnitude to the corresponding rates of reaction of nitrogen with niobium and tantalum: it is also similar in that the nitride film dissolves in the metal as fast as it is formed. Figs. 24 and 25 show the effect of temperature and pressure respectively on the reaction rate. The reaction of nitrogen with titanium, zirconium, niobium and tantalum follows the parabolic rate law and so also does the corresponding vanadium reaction; the values of the rate constant K in the equilibrium $W^2 = Kt + C$ are as follow:

°C.	600	650	700	800	900
K (g./cm.^{2})^2	$2{\cdot}61 \times 10^{-13}$	$3{\cdot}97 \times 10^{-13}$	$7{\cdot}08 \times 10^{-13}$	$3{\cdot}75 \times 10^{-12}$	$1{\cdot}50 \times 10^{-11}$

The energy of activation in the temperature range 0–900°C. is 31,400 g.-cal./mole. It was also observed that the nitride is stable up to at least 1000°C.

Some values for the molal heat capacity of vanadium nitride (VN) at low temperatures are as follow[12]:

T°K.	52·6	80·0	104·5	155·5	205·8	256·1	298·16
C_p g.-cal./deg.	1·272	2·688	3·809	5·759	7·244	8·379	9·080

Other work on the heat capacity and entropy of VN has been reported and some smoothed values are given below:

T°K.	400	600	1000	1,300	1,600
$H_T - H_{298 \cdot 16}$ g.-cal./mole	1010	3200	8130	12,090	16,200
$S_T - S_{298 \cdot 16}$ g.-cal./deg./mole	2·91	7·34	13·60	17·06	19·90

King[13] derives the specific heat equation:

$$C_p = 10 \cdot 94 + 2 \cdot 10 \times 10^{-3} T - 2 \cdot 21 \times 10^5 T^{-2}$$

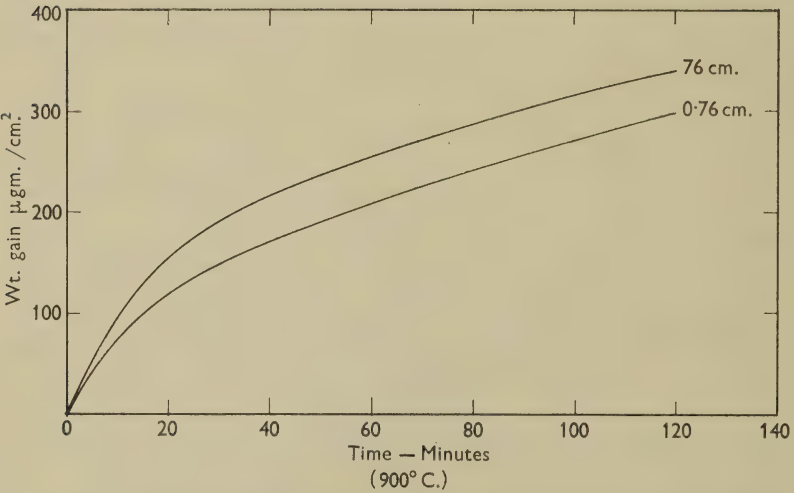

FIG. 25.—Effect of pressure on the reaction of nitrogen with vanadium

He says that the heat content data reported by Satô[6] deviate from the above and merit no comparison. Kelley[14] gives the heat and free energy of formation as $\Delta H_{298 \cdot 1} = -41 \cdot 43$ kcal./mole and $\Delta F^{\circ}_{298 \cdot 1} = -35 \cdot 06$ kcal./mole.

The entropy of VN at 298·16 is given by: $S^{\circ}_{298 \cdot 16} = 8 \cdot 91 \pm 0 \cdot 04$ (e.u./mole). The entropy of formation from the elements is $\Delta S^{\circ}_{298 \cdot 16} = 21 \cdot 0 \pm 0 \cdot 1$.

The electrical resistivity of vanadium nitride is 0·859 and $0 \cdot 599 \times 10^{-4}$ ohm-cm. at room and liquid air temperatures respectively. A room temperature value of $3 \cdot 32 \times 10^{-4}$ ohm-cm. has also been reported.[3]

The transition temperature for super-conductive vanadium nitride is reported as 8·2°,[16] 7·5°K.[17] and 1·3°K.[18] The first value is the most recent and more likely to be accurate.

Some measurements have been made on vanadium nitride to determine the neutron-scattering cross-sections of nitrogen and vanadium.[19]

Dumas' method and decomposition with potassium hydroxide are not satisfactory for the determination of vanadium nitride.[26] Addition of potassium sulphate is recommended in using the Kjeldahl process.[27]

Niobium Nitrides

Pure niobium nitride (NbN) was prepared by Duwez and Odell[7] by direct nitriding of niobium metal powder with nitrogen at 1200°C. Using the same method Brauer *et al.*[28] found that temperatures of 1300–1450°C. were necessary, but in other work a temperature of 1000°C. was sufficient.

Using a continuous flow method, crystalline niobium nitride can be deposited from $NbCl_5$ vapour in the presence of nitrogen and hydrogen on a heated tungsten filament.[29] With an optimum filament temperature of 1340–1360°C., small silver-grey crystals are obtained.

The powdered pentoxides of niobium and tantalum can be separated by nitriding at 500–800° with ammonia or at a little below 900° with nitrogen and hydrogen. Niobium nitride is produced if the reaction proceeds quickly, but little or no tantalum nitride.[61]

If a compressed mixture of niobium nitride with an equivalent amount of niobium is heated at 1700° for 15 min., pale grey metallic Nb_2N is formed. This substance is also formed if Nb_2O_5 is heated in a current of hydrogen containing some nitrogen at temperatures between 1300° and 1700°C.[30] or if niobium wire is heated in ammonia at 1400–1800°.[31] Its heat of formation at 298°K. is $-61{\cdot}1$ kcal.[82]

The solubility of nitrogen in the niobium lattice is very small; Brauer and Jander[32] found that up to about 2 atoms of nitrogen would dissolve, with a consequent increase in the lattice constant from $a = 3{\cdot}301$ A. to $a = 3{\cdot}303$ A. giving the so-called α phase. Other phases have been obtained by nitriding niobium metal powder or niobium hydride with dry oxygen-free ammonia at various temperatures between 700° and 1100°C. for periods varying between 1 hour and 2 weeks. A β phase corresponding to the composition range $NbN_{0{\cdot}40}$–$NbN_{0{\cdot}50}$ (i.e. Nb_2N) was found to be of the common 'interstitial' structural type with the metal atoms hexagonally close-packed.[27] The unit cell dimensions vary from $a = 3{\cdot}056$ A., $c = 4{\cdot}956$ A., $c/a = 1{\cdot}622$($NbN_{0{\cdot}40}$) to $a = 3{\cdot}048$ A., $c = 4{\cdot}995$ A., $c/a = 1{\cdot}639$($NbN_{0{\cdot}50}$), whilst Umanski[34] reports values of $a = 3{\cdot}017$ A., $c = 5{\cdot}580$ A. for $NbN_{0{\cdot}50}$. Rundle from theoretical considerations states that the nitride referred to in some work as NbN is really Nb_2N. Schönberg found that powder photographs of nitrides with a composition varying over the range $NbN_{0{\cdot}50}$–$NbN_{0{\cdot}86}$ showed, besides the pattern of the β phase, diffraction lines of a new phase (γ). A sample with the composition $NbN_{0{\cdot}86}$ contained this phase in a pure state. The γ phase, with a homogeneity range $NbN_{0{\cdot}80}$–$NbN_{0{\cdot}90}$, was found to be isomorphous with the δ phase in the TaN system (which has the tungsten carbide, WC, structure). The unit cell dimensions vary between $a = 2{\cdot}950$ A., $c = 2{\cdot}772$ A., $c/a = 0{\cdot}940$ and $a = 2{\cdot}958$ A., $c = 2{\cdot}779$ A., $c/a = 0{\cdot}939$; the most likely position of the nitrogen atom is at one of the centres of the two trigonal metal atom prisms in the unit cell. In the region $NbN_{0{\cdot}75}$–$NbN_{0{\cdot}94}$ the existence of two phases is reported[23, 27]: $NbN_{0{\cdot}75}$–$NbN_{0{\cdot}79}$ with a tetragonally deformed NaCl structure and $NbN_{0{\cdot}87}$–$NbN_{0{\cdot}94}$ with NaCl structure. Schönberg was unable to observe traces of these phases in *X*-ray photographs and considered that these nitrides were in reality phases of the Nb–N–O system. A fourth phase observed by both Schönberg ('δ-phase') and Brauer[27] ('NbN II' phase) has the approximate composition $NbN_{0{\cdot}95}$. This has a hexagonal close-packed structure, the dimensions of the unit cell being $a = 2{\cdot}968$ A., $c = 5{\cdot}535$ A., $c/a = 1{\cdot}865$; the nitrogen atoms are probably located at the centres of the metal atom octahedra. A fifth phase which is the richest in nitrogen has the composition $NbN_{1{\cdot}00}$ (this is called ϵ phase by Schönberg and 'NbN I' phase by Brauer). It has a hexagonal lattice; the constants of the unit cell, which contains 4 NbN molecules, are $a = 2{\cdot}952$ A., $c = 11{\cdot}25$ A. and $c/a = 3{\cdot}811$.

Schönberg points out that the M–N systems with M = V, Nb or Ta exhibit great similarities for low nitrogen contents, but discrepancies for high nitrogen contents. The solubility of nitrogen in the metal lattice is of the order of 2 atom-%. The 'interstitial' structure type, M_2N, with the metal atoms hexagonally close-packed and the nitrogen atom in one of the two metal atom octahedra of the unit cell, is common for the three M–N systems. This phase has a comparatively broad homogeneity range with the upper phase limit closely corresponding to the composition M_2N. Furthermore it is highly probable that a continuous solid solution series V_2N–Nb_2N–Ta_2N exists. The $NbN_{0\cdot8-0\cdot9}$ and $TaN_{0\cdot8-0\cdot9}$ phases are isomorphous, whilst no analogous V–N phase exists. The atomic grouping for the ϵ phase in the NbN system can be regarded as a transitional state between the arrangements of atoms in the γ and δ phases. VN and NbN are of the NaCl and γ^1 MoC types respectively. The structure of TaN is of the *B*35 type ('structurbericht').

As indicated above, confusion has arisen over structures described as nitrides, but in reality phases in the Nb–N–O system. Schönberg has made some studies of this system. Ammonia nitriding of niobium oxides or ammonium niobate leads to the formation of a phase with an NaCl type structure. The composition of this phase was found to vary slightly about the approximate composition $NbN_{0\cdot90}O_{0\cdot1}$. The same compound was also obtained by the oxidation of NbN (γ or ϵ) with steam in the presence of a great excess of hydrogen at a temperature of about 700°C. This oxidation process also gave rise to a phase with a tetragonally deformed NaCl structure. The same compound was obtained if $NbN_{0\cdot8-0\cdot9}$ (γ) was used as a starting material. The composition of this oxide-nitride was found to vary between the approximate limits $NbN_{0\cdot6}O_{0\cdot2}$ and $NbN_{0\cdot6}O_{0\cdot3}$. No other ternary metallic phases seem to exist in the Nb–N–O system, as oxidation of nitrides with steam for prolonged periods only leads to the formation of already known niobium oxides.

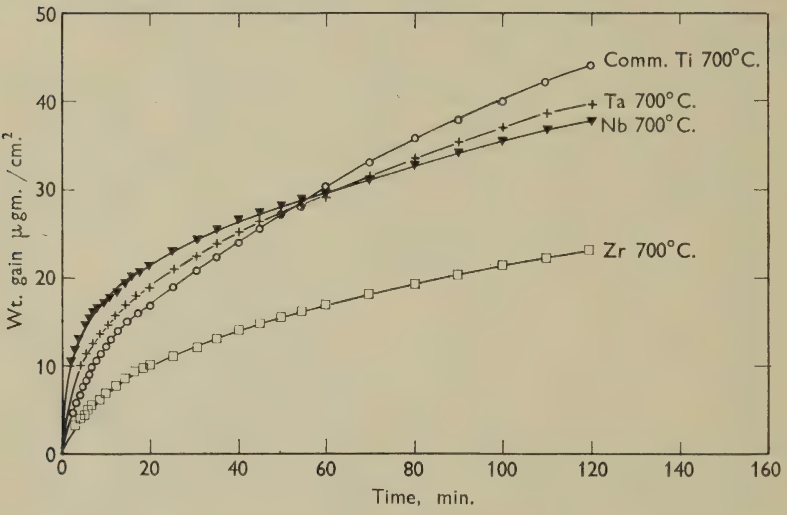

FIG. 26.—Absorption of nitrogen by zirconium, niobium, tantalum and titanium

The effect of temperature and pressure with time on the reaction of nitrogen with niobium[36] has been investigated. Fig. 26 shows the absorption curve for 700°C.; the curves for tantalum, zirconium and titanium are also given for comparison. Fig. 27 shows the effect of temperature on the reaction between niobium and nitrogen. The reaction, like that of tantalum, zirconium and titanium, follows the parabolic rate law; Table II gives the parabolic rate law constants.

Table II.—Parabolic Rate Law Constants for the Reaction between Niobium and Nitrogen

Temperature, °C.	K (g. per cm.^{2})^2 sec.$^{-1}$
400	$1{\cdot}55 \times 10^{-15}$
500	$5{\cdot}55 \times 10^{-15}$
600	$2{\cdot}97 \times 10^{-14}$
700	$1{\cdot}512 \times 10^{-13}$
800	$5{\cdot}42 \times 10^{-13}$

The data deviate slightly from the parabolic law in the early stages of the reaction. However, by using the method of Van Liempt it has been shown that the parabolic rate law follows from consideration of direct diffusion of nitrogen into the metal. From the data in Table II an energy of activation of 25,400 g.-cal./mole is calculated. The negligible effect of pressure is similar to that found for the tantalum reaction (see Fig. 29). In vacua of 10^{-6} mm. Hg or lower the niobium–nitrogen product loses weight below 605°C., while at higher temperatures the metal acts as a 'getter' in a similar manner to tantalum and zirconium. It would seem that the reaction does not take place directly on the metal, but rather through a film of nitride which hinders the pressure from exerting its normal influence on this type of reaction. The nitride film thickness is governed by the rate of formation and the rate of solution.

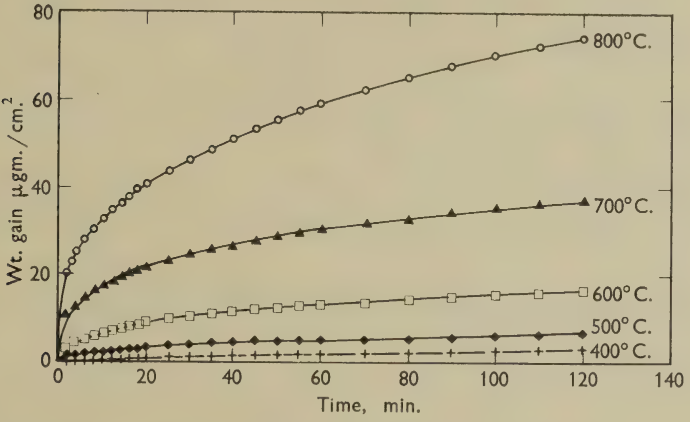

FIG. 27.—Effect of temperature on the absorption of nitrogen by niobium

The heat of activation for diffusion of nitrogen in niobium is 39·500 kcal./mole.[37]

On increasing the nitrogen content of niobium from 42 to above 46·5 atom-%, the electrical resistivity at 20°C. increases from 3 to 10×10^{-5} ohm; for the same nitrogen increase the ratio of the resistivities at 20·4 and 293°K. increases from 0·25 to 1·18, whilst the transition temperature for super-conductivity increases from 11° to 14·2°K.[38] The transition temperature varies with the nitrogen content, viz. 16·2°K. to 13·5°K. corresponding to nitrogen contents of 11·1 to 12·8%.[39] Horn and co-workers[40] observed a transition temperature of 15·2°K. for NbN, while Hulm and Matthias[41] report values of 14·7°K. for NbN and 9·5°K. for Nb_2N. Aschermann *et al.*[42] give 16°K. as the transition temperature. Other work relating to the use of niobium nitride in superconductivity studies is reported.[43–58]

Some values of the low-temperature heat capacity of niobium nitride are as follow[59]:

T°K.	C_p (g.-cal.deg.$^{-1}$ mole^{-1})
11·00	0·0396
12·00	0·0468
14·00	0·0791
15·00	0·0874
17·00	0·0983
20·00	0·1535

The author states that there is an anomaly of 0·023 g.-cal./mole^{-1} at 15°K. The specific heat of NbN over the temperature range 0–300°C. can be represented by the equation

$$c = 0{\cdot}0963 + 3{\cdot}264 \times 10^{-5} t \quad ^{60}$$

Studies have been made of the effects of the presence of niobium nitrides on some physical properties of steel.[62–67]

Tantalum Nitrides

The vapour phase deposition of tantalum nitride (TaN) from tantalum pentachloride vapour, nitrogen and hydrogen on a heated tungsten filament is described[8]; filament temperatures of about 1600°C. are required to prevent the undesired deposition of metallic tantalum in the presence of hydrogen.

The nitride TaN can be prepared also by causing tantalum metal to react with nitrogen or ammonia; Chiotti[68] found it necessary to pass ammonia for 18 hours over the metal powder or shavings at 900°C., and even this procedure does not give complete conversion to the mononitride.

If the powdered pentoxide reacts with ammonia at 500–800°C., or with nitrogen and hydrogen at about 900°C., little or no TaN is formed.[61] Moers[8] mixed the pentoxide with lampblack and then caused the mixture to react with nitrogen at 2300°C.

The nitride 'Ta_3N_5' can be prepared from Ta_2O_3 by first heating the oxide with a slight excess of CaH_2 to produce the metal, and then treating this with nitrogen or ammonia; the presence of CaO formed during the reduction process prevents the nitride particles fusing together.[68]

Liquid ammonia reacts with tantalum pentachloride forming a mixture of $Ta(NH_2)_2Cl_3{,}7NH_3$ and $NH_4Cl{,}3NH_3$. On heating this mixture in a vacuum to 170°C. the $NH_4Cl{,}3NH_3$ and NH_3 are expelled leaving a residue of yellow $Ta(NH_2)_2Cl_3$. When $Ta(NH_2)_2Cl_3$ is heated in the presence of ammonia, 'Ta_3N_5' is formed; on heating in a vacuum TaN and a volatile Ta compound of undetermined composition are produced. At high temperatures Ta_3N_5 decomposes, forming the mononitride and nitrogen.[69]

Schönberg[70] prepared various tantalum nitrides by causing ammonia to react with tantalum powder or its hydride at temperatures of 700–1100°C. Four intermediate nitride phases were thus obtained[1]:

(1) A β phase, representing the solubility of nitrogen in tantalum, approximating in composition to $TaN_{0{\cdot}05}$, in which the tantalum atoms occupy a body-centred cubic sub-lattice having an edge $a = 3{\cdot}369$ Å. The diffraction data could be explained on the basis of a cubic super-lattice having a cubic edge three times as long as the sub-lattice edge, i.e. $a = 10{\cdot}11$ Å.; the exact structure has not yet been determined.

(2) A γ phase, ranging in composition from approximately $TaN_{0{\cdot}40}$ to $TaN_{0{\cdot}45}$ with the metal atoms in a close packed hexagon. This corresponds closely to the formula Ta_2N: for the homogeneity range the unit cell dimensions are: $a = 3{\cdot}041$ to 3·048 Å., $c = 4{\cdot}907$ to 4·918 Å., $c/a = 1{\cdot}614$.[71, 72]

(3) A γ phase which has a homogeneity range of about 3 atom-% of nitrogen within the limits $TaN_{0{\cdot}80}$–$TaN_{0{\cdot}90}$, the metal atoms forming a simple hexagonal lattice. Brauer and Zapp[71, 72] found no such compound.

(4) An ϵ phase which is homogeneous at the stoicheiometric composition TaN; it has a hexagonal unit cell with $a = 5{\cdot}185$ A., $c = 2{\cdot}908$ A., $c/a = 0{\cdot}561$. This structure is identical with that found by Brauer and Zapp, and the unit cell contains 3 molecules of TaN.

The tantalum nitride 'TaN' of Horn and Ziegler,[40] which was considered to have a complex structure, is not in any way related to the δ or ϵ phases of Schönberg as shown by *X*-ray diagrams: the diffraction lines and intensities do, however, agree well with those observed for ternary Ta-N-O phases.

The compound corresponding to the formula TaN as prepared by van Arkel (Mellor, VIII, 126), which was reported to have a hexagonal wurtzite lattice, was shown to be analogous to the compound Nb_2N prepared by Brauer; furthermore it had almost the same unit cell dimensions.

Chiotti[68] considered that the compound referred to by van Arkel as TaN is in fact Ta_2N; this was later confirmed by analysis. The same conclusion had also been reached by Rundle[35] from theoretical considerations. Brauer and Zapp[71, 72] report that the tantalum–nitrogen system consists only of 3 phases: TaN, Ta_2N and Ta. These phases were studied by heating the elements at 1400°C.

The metal phase is homogeneous in the range Ta–$TaN_{0{\cdot}04}$.

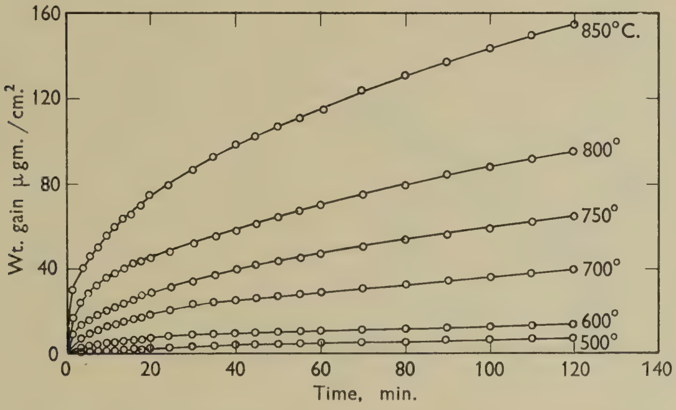

FIG. 28.—Reaction of tantalum with nitrogen: effect of temperature

The 'Ta_2N' phase has a homogeneity range of $TaN_{0{\cdot}50}$–$TaN_{0{\cdot}41}$; the structure is hexagonal with unit cell dimensions of $a = 3{\cdot}042$ kX., $c = 4{\cdot}909$ kX., $c/a = 1{\cdot}61$; the density is 15·46 g./c.c. The 'TaN' phase has a homogeneity range of TaN to $TaN_{0{\cdot}99}$. It has a hexagonal structure with lattice constants $a = 5{\cdot}1808$ kX., $c = 2{\cdot}9049$ kX. and $c/a = 0{\cdot}561$. The nitrogen atoms fit into the cavities of the metal lattice, each being surrounded by six tantalum atoms. The Ta–N distance is 2·08 or 2·59 kX., each tantalum atom being surrounded by six nitrogen atoms. The calculated density is rather higher than the pycnometric density of 13·70.

Filaments of tantalum when heated at 3400°K. in low pressure nitrogen absorb up to 100 volumes of nitrogen; at this point the equilibrium pressure falls and further absorption can occur up to the formation of TaN. At 700°C. and 1 micron pressure nitrogen is absorbed on a tungsten filament; above 1000°C. there is a rapid increase in absorption.[73] The effect of temperature and pressure with time on the reaction between tantalum and nitrogen has been studied using the vacuum microbalance method. Fig. 28 shows the absorption curve at 700°C.; the curves for niobium, zirconium and titanium are also given for comparison in Fig. 26. Fig. 28 shows the effect of temperature on the reaction between tantalum and nitrogen, whilst Fig. 29 shows the effect of pressure on the same reaction. The reaction, like that of zirconium, titanium and niobium, follows the parabolic rate law, i.e., $W^2 = kt + c$

where W is the weight of nitrogen absorbed in time t, c and k being constants. Table III gives the parabolic rate law constants.

Table III.—Parabolic Rate Law Constants for the Reaction between Tantalum and Nitrogen

Temperature, °C.	k (g./cm.^{2})^2 sec.$^{-1}$
500	$9{\cdot}6 \times 10^{-15}$
600	$1{\cdot}78 \times 10^{-14}$
700	$1{\cdot}89 \times 10^{-13}$
750	$5{\cdot}28 \times 10^{-13}$
800	$1{\cdot}14 \times 10^{-12}$
860	$2{\cdot}94 \times 10^{-12}$

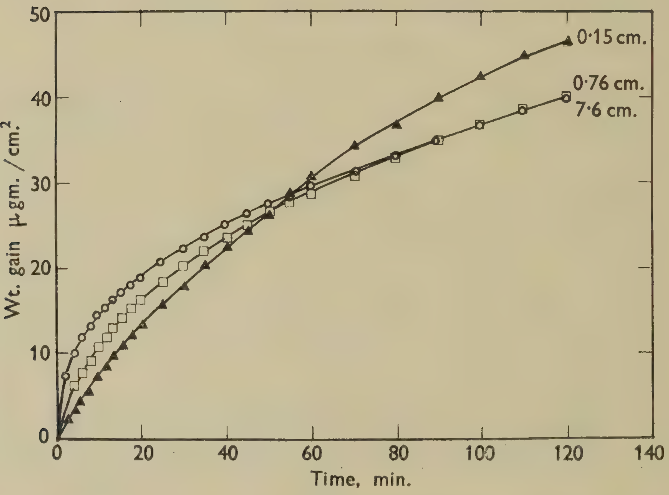

Fig. 29.—Reaction of tantalum with nitrogen at 700°C.; effect of pressure

The data deviate slightly from this law in the early stages of the reaction. It is interesting to note, however, that with the method of van Liempt the parabolic rate law could be deduced directly from the diffusion of nitrogen into the metal. From the data in Table III an energy of activation of 39,400 g.-cal./mole is calculated. The heat of activation of diffusion of nitrogen in tantalum is 39,800 g.-cal./mole.[37]

In a vacuum of 10^{-6} mm. or lower the tantalum–nitrogen product loses weight below 605°C., while at higher temperatures the metal acts as a 'getter' in a similar manner to zirconium and niobium.

Fig. 29 shows that despite a fifty-fold variation the effect of pressure is small. It would seem that the reaction does not take place directly on the metal, but rather through a film of nitride which prevents the normal influence of pressure. The nitride film thickness is governed by the rate of formation and the rate of solution of nitrogen.

Tantalum mononitride does not become super-conductive until it reaches a temperature of 1·88°K., whilst the transition temperature for Ta_2N is 9·5°K.[16, 40, 41, 74]

The mean specific heat of tantalum mononitride over the temperature range 0–500°C. can be expressed by the equation:

$$c = 0{\cdot}04785 + 7{\cdot}068 \times 10^{-5}t - 5{\cdot}808 \times 10^{-8}t^2$$

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Using this expression, the heat of formation at 25°C. is calculated as 58·65 kcal./mole,[75] while Neumann *et al.*[76] give $\Delta H = -58{\cdot}1$ kcal./mole. Kelley[14] accepts this value and calculates an entropy of formation of $\Delta S_{298\cdot 1} = 12{\cdot}4$ and a free energy of formation of $\Delta F^{\circ}_{298\cdot 1} = -52{\cdot}17$ kcal./mole. More recent work gives $\Delta H = -60{\cdot}0$ and $\Delta F = -53{\cdot}2$ kcal.[77] The standard energy of formation of Ta_2N at 298°K. is $-64{\cdot}7$ kcal.[82]

The specific resistance of the mononitride is $1{\cdot}35 \times 10^{-4}$ and $0{\cdot}000 \times 10^{-4}$ ohms/cm. at room temperature and at liquid air temperature, respectively.[8, 15]

Microhardness is reported[81] to be 3236 kg./sq. mm.

Schönberg[70, 78] has studied the phases formed by nitriding binary and ternary Ta–M alloys (M = Ti, V, Cr, Mn, Fe, Co, Ni) with dry ammonia at temperatures varying between 650° and 950°C. Ternary phases (see below) were found to exist in the Ta–M–N systems where M = Cr, Mn, Fe, Co, Ni but not with M = Ti, V.

The Ta_3MnN_4 system is hexagonal with four metal atoms in the unit cell. The three $Ta_2MN_{2\cdot 5}$ (M = Fe, Co, Ni) have very similar hexagonal structures but show super-structures containing twelve metal atoms in the unit cell. The metals iron, cobalt and nickel can replace each other in all proportions.

The metal atoms in the phases Ta_3MnN_4 and $Ta_2(Fe, Co, Ni)N_{2\cdot 5}$ occupy a close-packed arrangement designated by the sequence AB, AC, AB, AC. The phases $(Ta,Cr)N_x$ and $(Ta,Mn)N_x$, which have ratios Ta:Cr and Ta:Mn probably close to unity, are isomorphous, but the structure and composition are unknown.

The nitrides of the metals M were found to be insoluble in the ϵ phase of tantalum mononitride. Up to about 10% of the tantalum atoms in $TaN_{0\cdot 80-0\cdot 90}$ (δ phase) can be replaced by manganese atoms thus causing a comparatively strong deformation of the simple hexagonal lattice. The TiN, VN and CrN phases of sodium chloride type have been found to form solid solutions with the TaN phase up to the approximate limits 10, 20 and 25 atom-% of TaN respectively. No solubility of tantalum in the most nitrogen-rich nitrides of manganese and iron has been observed. Schönberg[79] has also studied the phases formed in the system Ta–N–O. Four metallic ternary phases were obtained with the approximate compositions $TaN_{0\cdot 90}O_{0\cdot 10}$, $TaN_{0\cdot 75}O_{0\cdot 10}$, $TaN_{0\cdot 75}O_{0\cdot 25}$, $TaN_{0\cdot 65}O_{0\cdot 35}$ and $TaN_{0\cdot 50}O_{0\cdot 50}$. A similar study of the Ta–C–N system showed that the ternary phases do not exist. A limited amount of work has been done on the Ta–Si–N system.[80]

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NITRIDES OF GROUP VI METALS

Chromium Nitrides

PREPARATION

Chromium nitride, CrN, can be prepared by the direct combination of nitrogen and chromium at 900°C. and 25 atm.[1, 2] Both Cr_2N and CrN are formed in the reaction between chromium borides and dry ammonia[3]; CrN only is obtained at 735°C.; both CrN and Cr_2N are produced between 800° and 1100°C. whilst only Cr_2N is formed at 1180°C. By treating chromium with ammonia at 900°C. needles of Cr_2N are obtained.[4] Cr_2N is probably formed in the thermal decomposition of $Cr(NH_2)_3$ at temperatures above 320°C.[5]

THE CHROMIUM–NITROGEN SYSTEM

The two nitrides of chromium, Cr_2N and CrN, are now well-established compounds. Yamaguchi *et al.*[21] report that after treatment with ammonia at 300–350°C. and at 2 atm. for 2 hours, chromium steel, under an electron beam, shows the diffraction patterns of Cr_3N. Valensi[6, 7] reports that the dissociation of chromium nitride is analogous to that of vanadium hydride, and that CrN can absorb small quantities of nitrogen; it is also soluble in chromium, especially at higher temperatures. According to Blix *X*-ray analysis of a series of chromium–nitrogen products prepared by heating electrolytic chromium in a stream of ammonia at 800°C. reveals the existence of two intermediate phases in the Cr–N system.[8] One of these, corresponding to Cr_2N, remains homogeneous over a wide concentration range, including 33 atom-% of nitrogen and the chromium atoms of this phase are arranged in a hexagonal close-packed lattice, whilst the nitrogen atoms are probably randomly arranged in the interstices. The lattice dimensions increase with increasing nitrogen content from $a=2{\cdot}747$ A. and $c=4{\cdot}439$ A. to $a=2{\cdot}770$ A. and $c=4{\cdot}474$ A. According to Eriksson[9] this hexagonal phase (Cr_2N) has a 'super-structure' with a volume three times that of the close-packed hexagonal lattice: the length of the c axis is the same for both unit cells, but that of the a axis is 1·732 times that of the close-packed lattice; the homogeneity limits are 11·9–9·3% of nitrogen. The dimensions range from $a=4{\cdot}750$ A. (2·742 A), $c=4{\cdot}429$ A. (4·429 A.) and $c/a=0{\cdot}933$ (1·615) at the lower limit to $a=4{\cdot}796$ A. (2·769 A.), $c=4{\cdot}470$ A. (4·470 A.) and $c/a=0{\cdot}932$ (1·614) at the upper limit, the numbers in parentheses referring to the close-packed hexagonal cell.

The other phase observed by Blix[8] corresponds to CrN and has the cubic sodium chloride structure with a lattice parameter of 4·140 A. This author also observed that in the *X*-ray photographs of ferro-chrome metal (with 60·3% of chromium, 2·4% of nitrogen, 2·0% of silicon and 0·21% of carbon) there appeared among other patterns those of the hexagonal Cr–N phase; thus it is probable that the nitrogen

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of ferro-chromium exists in this phase. The solubility of nitrogen in solid chromium was also shown to be small.

The effect of pressure on the composition of the solid solution of nitrogen in chromium as a function of temperature has been studied[10]; this was in an investigation of the reaction:

$$N + 2Cr(s) \rightleftharpoons Cr_2N(s)$$

where N is the nitrogen in solid solution; Fig. 30 shows the nitrogen solubility curve thus obtained. From the results it is calculated that the heat of decomposition of r_2N to the saturated solid solution is 28,500 g.-cal./mole as compared with 8000 g.-cal./mole for the corresponding decomposition of Fe_4N; the enthalpy of formation of Cr_2N is $-23{,}500$ g.-cal./mole as compared with a value of $-2{,}600$ g.-cal./mole for Fe_4N. The heat absorbed by the solution of nitrogen into either of the two body-centred cubic solvents (i.e. Cr_2N and Fe_4N) is about the same, i.e. $+5000$ g.-cal./g.-atom of nitrogen. Seybolt and Oriani[10] state that the uniformity of ΔH is in keeping with the very similar lattice parameters of the two metals and with the similar nature of the electronic orbitals about the closed shells in the separated atoms, viz., $(3d)^6\,(4s)^2$ for iron and $(3d)^5\,(4s)^1$ for chromium, whence the electronic distribution about the nitrogen is essentially the same in both the Fe(N) and Cr(N) solid solutions. With regard to the compounds themselves, the situation is very different; Cr_2N and Fe_4N, as already mentioned, differ markedly in enthalpy of formation and in stability. The most likely sites for the interstitial solute atoms are

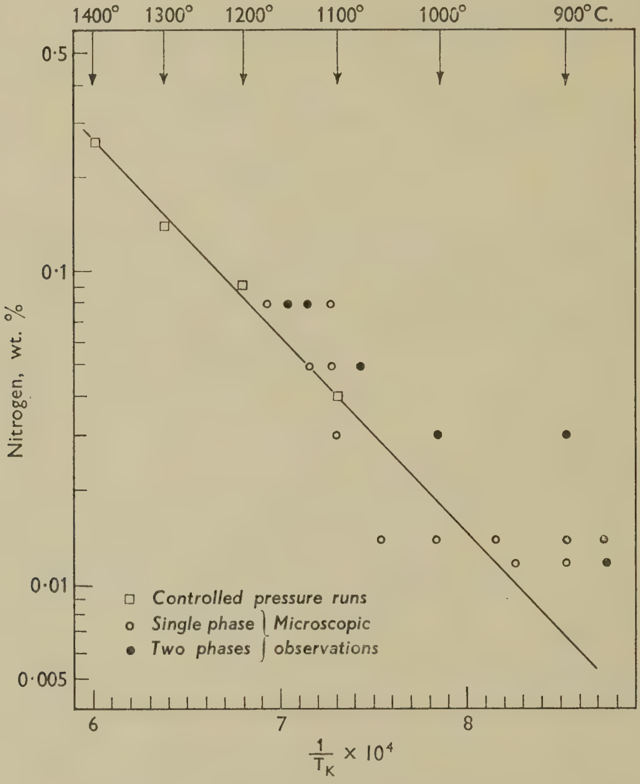

FIG. 30.—Solid solubility of nitrogen in chromium

the octahedral interstices in both the face-centred cubic Fe_4N and the close-packed hexagonal Cr_2N lattice structures. Both possess one octahedral hole per substitutional lattice site, so that the nitrogen atoms occupy one-quarter of the available holes in Fe_4N and one-half in Cr_2N. The radii of these octahedral holes are calculated to be 1·89 A. and 2·13 A. for Fe_4N and Cr_2N respectively. Hence the smaller volume available for the nitrogen in Fe_4N is responsible for the much lower stability of Fe_4N.

SOLUBILITY OF NITROGEN IN CHROMIUM

Nitrogen has a marked effect on the melting point of chromium. In an investigation of the solubility of nitrogen in liquid chromium,[11, 12] it was shown that the equilibrium concentration of nitrogen in wt.-% is 4·08 at 1600°C., 3·90 at 1650°C., 3·84 at 1700°C., 3·76 at 1725°C. and 3·54 at 1750°C. These data indicate that the interaction of liquid chromium and nitrogen occurs according to the equation $2Cr+\frac{1}{2}N_2 \rightarrow Cr_2N$, for which the free energy change is given by $\Delta F = -7594{\cdot}5 + 1{\cdot}2727T$. *X*-Ray analysis of the high-nitrogen specimen showed the presence of a body-centred cubic chromium phase and the Cr_2N phase with a close-packed hexagonal structure, $a = 2{\cdot}74 \pm 0{\cdot}002$ A., $c = 4{\cdot}45 \pm 0{\cdot}01$ A. The solubility of nitrogen (wt.-%) in chromium with various silicon contents and at various temperatures is given in Table IV.

Table IV.—Solubility of Nitrogen (wt.-%) in Chromium Containing Silicon

% of Silicon	1·5	7·25	10·0	20·0
1600°C.	3·83	1·98	0·84	0·33
1650°C.	3·68	1·89	0·74	0·30
1700°C.	3·54	1·72	0·69	0·28
1750°C.	3·08	1·68	0·62	0·26

At 1600°C. the solubility of nitrogen decreases with increasing silicon content up to 40% of silicon and no special effect for a 1 : 1 chromium–silicon compound was observed.

The solubility of nitrogen in liquid chromium and chromium–iron alloys is reported also by Brick and Creevy,[13] who find that the solubility in pure liquid chromium is 13·6 atom-%, the relation between solubility and pressure following Sievert's square root law, and the solubility decreasing with increase in temperature.

The relation between temperature and dissociation pressure of the two nitrides, CrN and Cr_2N, is given by the following equations[14]:

$$\log p_{N_2} = \left(-\frac{9558{\cdot}31}{T}\right) + 8{\cdot}103 \quad \text{for the reaction } Cr_2N = 2Cr + \tfrac{1}{2}N_2$$

and

$$\log p_{N_2} = \left(-\frac{12071{\cdot}35}{T}\right) + 10{\cdot}655 \quad \text{for the reaction } 2CrN = Cr_2N + \tfrac{1}{2}N_2$$

The heats of formation as calculated from the dissociation pressures of the two nitrides are: $\Delta H_{298} = -20{\cdot}602$ kcal./mole, for Cr_2N, and $\Delta H_{298} = -24{\cdot}298$ kcal./mole, for CrN. Satô[15] recalculated these values and found 26·340 kcal./mole for Cr_2N and 28·260 kcal./mole for CrN.

According to Neumann *et al.*,[1] the experimentally determined heat of formation of CrN is 29·5 kcal./mole, and the poor agreement between the experimental value and that calculated from dissociation data indicates that the dissociation pressures have not been determined sufficiently accurately to permit estimation of the influence of mixed crystal formation on the calculations. Valensi[6, 7] also suspected that solid solutions were formed in the decomposition reaction.

The free energies of formation are $\Delta F^{\circ}_{298} = -17{\cdot}262$ kcal./mole, for CrN, and $\Delta F_{298} = 19{\cdot}545$ kcal./mole for Cr_2N; entropy values are: $S_{298} = 22{\cdot}9$ g.-cal./degree, for Cr_2N; $S_{298} = 12{\cdot}6$ g.-cal./degree, for Cr_2N.[14]

Chromium mononitride is not superconductive down to a temperature of 1·2–1·3°K.[55]

The reader is referred also to the reviews of thermodynamic data given by Maier,[16] Kelley[17] and by Pearson and Ende.[18]

Nemnonov[19] critically surveyed the theories of the nature of bonds formed between transition metals and metalloids, especially between chromium and nitrogen, hydrogen, carbon, oxygen. He considers that the inter-atomic bonds in the chromium nitrides are not of metallic character but are homopolar as in the chromium carbides. The reader is referred also to the general discussion on the nature of the bonds in nitrides in the introduction.

Chromium–manganese alloys readily absorb nitrogen at high temperatures and in the range 20–65 wt.-% of manganese a white nitride phase is formed even at a low nitrogen pressure.[20] From *X*-ray diffraction studies it is suggested that the new substance is possibly a ternary alloy of the formula $(CrMn)_3N$.

Molybdenum Nitrides

PREPARATION

An *X*-ray investigation of the products of the action of nitrogen on molybdenum at temperatures between 400°C. and 1000°C. showed no indication of nitride formation,[22] but similar evidence indicates that Mo_2N is formed by molybdenum catalysts in the synthesis of ammonia, and the nitrides of molybdenum by the action of dry ammonia on molybdenum powder.[23] When heated for 4 hours at temperatures from 400–700°C. the amount of nitrogen in the product ranged from 0·77 wt.-% to 7·15 wt.-% or 5·1 atom-% to 34·6 atom-%, respectively. At temperatures above 725° the nitride formed tended to dissociate. Ghosh[22] has reported that the maximum nitrogen concentration was obtained after 4 hours at 760°C. By carrying out the nitriding reaction for periods up to 120 hours at 700°C. it was possible to prepare products with nitrogen contents of up to 48 atom-%. In the reaction of ammonia with molybdenum only the γ nitride is obtainable in a pure state at 850°C.: below this temperature mixtures of α, β and γ nitrides are formed.[22] Molybdenum nitride is also obtained from the action of anhydrous ammonia on heated finely powdered molybdenum oxide.[24] Molybdenum plate and wire annealed at 1400°C. absorb only very small quantities of nitrogen between 900° and 1200°C.[25] Unannealed molybdenum wire, however, absorbs much greater quantities of nitrogen. On cooling unannealed molybdenum wire that has dissolved nitrogen at higher temperatures, a nitride phase separates; this can be demonstrated microscopically and by *X*-rays.[25]

THE MOLYBDENUM–NITROGEN SYSTEM

A phase diagram (Fig. 31) of the molybdenum–nitrogen system has been constructed by Hägg[23] from *X*-ray measurements on the products obtained by treatment of the pure metal powder with ammonia at temperatures from 400°C. to 725°C. for periods of up to 2 days. The following phases were reported:

α phase representing the solubility of nitrogen in molybdenum, which is very small.

β phase which is stable only above 600°C. The homogeneous region lies at about 28 atom-% of N. The metal atoms form a face-centred tetragonal lattice with lattice constants $a = 4{\cdot}180$ Å., $c = 4{\cdot}016$ Å., $c/a = 0{\cdot}961$. The positions of the nitrogen atoms have not been ascertained.

γ phase at temperatures below 600–700°C. This phase has a narrow homogeneity range in the region of 33 atom-% of nitrogen corresponding to the formula Mo_2N. At higher temperatures the homogeneity range has a greater molybdenum content. The metal atoms form a face-centred cubic lattice with a lattice constant of $a=4{\cdot}155$–$4{\cdot}160$ A.

δ phase exists at about 50 atom-% of nitrogen, corresponding to the formula MoN. The metal atoms form a simple hexagonal lattice, the structure being isomorphous with MoC and WC, but weak extra lines in the *X*-ray diagram indicate the existence of a superlattice. The lattice parameters of this hexagonal phase are $a=2{\cdot}860$ A., $c=2{\cdot}804$ A., $c/a=0{\cdot}908$. According to Pauling *et al.*[26] the distance of 2·16 A. between molybdenum and nitrogen atoms in this phase agrees with the assumption of half bonds.

The work of Hägg has been confirmed in all respects by Schönberg.[27] For the δ phase (prepared by passing dry ammonia over fine molybdenum powder at 800°C. for a few hours and then lowering the temperature at a constant rate to 300°C. over a period of four weeks) the probable dimensions of the unit cell are $a=5{\cdot}725$ A., $c=5{\cdot}608$ A., $c/a=0{\cdot}980$. The unit cell is a superstructure containing 8MoN molecules. For the δ phase it is suggested that the non-metal atoms are situated at the centres of trigonal prisms of metal atoms.

The existence of the β (30·5 to 33·0 atom-% of nitrogen) and γ (35·7 atom-% of nitrogen) phases has been confirmed by Sieverts and Zapf,[25] who report also an additional molybdenum-rich phase. The phase having composition of Mo_3N_2 has been tentatively identified by Mathis.[28]

The heat of formation of MoN is $\Delta H = -16{\cdot}6$ kcal./mole.[29]

MoN becomes superconductive at 12°K. and Mo_2N at 5°K.[30]

The rate of diffusion of nitrogen through molybdenum is given in Table V.[32, 33]

Table V.—Rate of Diffusion of Nitrogen through Molybdenum at Various Temperatures

Pressure, mm.	Temperature, °K.	Rate c.c. N_2 (N.T.P.) diffusing/ sec./sq.cm./1 mm. thickness
130	1373	$0{\cdot}78 \times 10^{-7}$
130	1423	$1{\cdot}08 \times 10^{-7}$
130	1473	$2{\cdot}12 \times 10^{-7}$
130	1573	$6{\cdot}1 \times 10^{-7}$
130	1673	$10{\cdot}8 \times 10^{-7}$
130	1723	$16{\cdot}5 \times 10^{-7}$
130	1773	$20{\cdot}6 \times 10^{-7}$
4·4	1773	$0{\cdot}39 \times 10^{-6}$
22·0	1773	$1{\cdot}06 \times 10^{-6}$
40·5	1773	$1{\cdot}51 \times 10^{-6}$
67·0	1773	$1{\cdot}64 \times 10^{-6}$
79·5	1773	$2{\cdot}12 \times 10^{-6}$
86·5	1773	$2{\cdot}11 \times 10^{-6}$
130	1823	$44{\cdot}2 \times 10^{-7}$
130	1873	$51{\cdot}8 \times 10^{-7}$

Though the effect of temperature on the diffusion of nitrogen through molybdenum is represented by the exponential term of Richardson's equation, the effect of pressure is only approximately indicated. Experimental results are, however, represented accurately by Smithells and Ransley's equation:

$$D = k\sqrt{P}[aP/(1+aP)]$$

which allows for the fraction of surface covered by the adsorbed layer, according to Langmuir's isotherm, and reduces to Richardson's equation at high pressures.

The permeability constant P_0 for nitrogen–molybdenum is $8{\cdot}3 \times 10^{-2}$, with an energy of activation $E = 45{,}000$ g.-cal./g.-atom.[32, 33]

In the preparation of ternary alloys containing molybdenum, nitrogen and carbon by carbiding molybdenum nitrides, no ternary Mo–C–N phase could be produced from the $(\beta+\gamma)$ mixed nitrides.[24] The γ nitride does, however, react with carbon monoxide at temperatures above 700°C to form a ternary Mo–C–N phase.

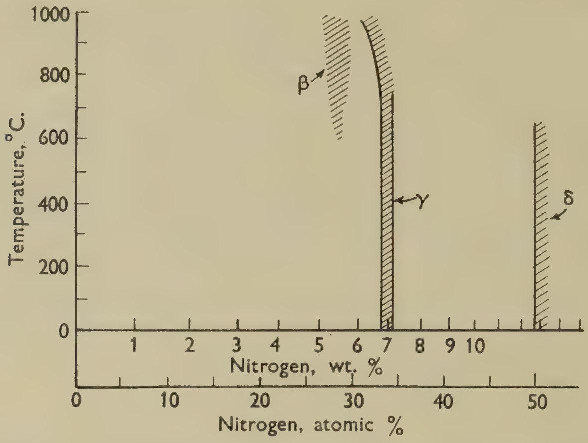

FIG. 31.—Phase diagram of the molybdenum–nitrogen system

Tungsten Nitrides

PREPARATION

Laffitte and Grandadam[35] confirm earlier work showing that no reaction takes place between tungsten and nitrogen at temperatures up to 900°C., whereas the reaction with ammonia starts at 140°C.

The brown deposit formed in the bulbs of nitrogen-filled tungsten lamps is reported to be the nitride WN_2,[36] which confirms the earlier work of Langmuir (Mellor, VIII, 129). This compound has not, however, been identified by Hägg or Schönberg (see below).

Sokols'kaya,[37] measuring nitride layers on a cylindrical anode when a tungsten filament is heated in nitrogen, found that at pressures of nitrogen above 5×10^{-1} mm. the layer formed is pure tungsten nitride, but at lower pressures it is a mixture of the nitride with tungsten.

Messner and Frankenburger[38] observed that in the catalytic synthesis of ammonia a surface film of nitride is formed.

In their studies of the W–N system, Hägg[23] and Schönberg[27] treated tungsten powder with ammonia at about 800°C. Kiessling and Liu[3] also prepared tungsten–nitrogen compounds in a similar manner.

THE TUNGSTEN–NITROGEN SYSTEM

The phases of the tungsten–nitrogen system have been ascertained by Hägg[23] from *X*-ray studies of the various phases prepared by treating the pure metal powder with ammonia at temperatures between 700° and 800°C. They are:

α phase (tungsten phase), corresponding to the solubility of nitrogen in tungsten, which is extremely small.

β phase ('W_2N'), having a face-centred cubic lattice ($a = 4{\cdot}126$ A.) and isomorphous with Mo_2N (γ phase). This phase was also identified tentatively by Mathis[28] and confirmed by Schönberg.[27]

A third phase (δ phase) (also found by Schönberg) which has a composition close to the formula WN; as it was not possible to prepare this compound in the pure state its exact composition is not known. This phase is isomorphous with tungsten carbide (WC) and it is less stable than the corresponding nitride of molybdenum, MoN; the metal atoms are arranged in a simple hexagonal lattice with the lattice constants $a = 2{\cdot}893$ A., $c = 2{\cdot}826$ A. and $c/a = 0{\cdot}977$. This compound decomposes in vacuo at 600°C. to form W_2N.

A second W_2N phase (γ) has been reported by Kiessling and Liu.[3] This material, formed by nitriding tungsten with ammonia at temperatures between 825°C. and 875°C., has a cubic lattice with the length of the unit cell varying between the limits $a = 4{\cdot}130$ A. at 825°C. and $a = 4{\cdot}122$ A. at 875°C. The evidence for this structure is not entirely satisfactory; Schönberg was unable to confirm its existence. Later work by Kiessling and Peterson[39] showed that this γ phase is an oxide-nitride. This phase has a defective nitrogen lattice but the vacancies are ordered; its ideal formula is $W_{0\cdot75}(N,O)_{1\cdot00}$ where the ratio N:O is unknown.

A further nitride, W_3N_2, has also been tentatively identified by Mathis.[28]

In addition to the oxide-nitride mentioned above a similar compound close to the formula $W_{0\cdot62}N_{0\cdot62}O_{0\cdot38}$ was prepared by Kiessling[39] by reducing ammonium paratungstate or tungstic oxide with ammonia. It has a defective metal–non-metal lattice with the sodium chloride structure; only 62% of the metal positions are statistically occupied by tungsten atoms, whereas probably all the non-metal positions are occupied, 62% by nitrogen atoms and 38% by oxygen atoms.

Hardy and Hulm[40] found that the nitride W_2N was not super-conducting even down to a temperature of about 1·20°K.

Uranium Nitrides

PREPARATION

The uranium–nitrogen system has been carefully investigated by Rundle *et al.*[41] Uranium mononitride, UN, was prepared by the thermal decomposition of higher nitrides of uranium in a vacuum, or by strongly heating mixtures of uranium and the higher nitrides, the reduction of higher nitrides with hydrogen, the direct reaction of ammonia or nitrogen with uranium hydride or the direct reaction between nitrogen and uranium. The higher nitrides were prepared by the direct reaction between either nitrogen or ammonia with the hydride or the metal, and by the reduction of still higher nitrides with hydrogen. The dinitride was prepared only at pressures of about 120 atm.[41]

THE URANIUM–NITROGEN SYSTEM

Nitrides of uranium having the formulæ U_3N_4, U_5N_2 and U_5N_4 were reported earlier (Mellor, VIII, 130), but according to Rundle *et al.*[41] the only phases in the system uranium–nitrogen are the three nitrides UN_2, U_2N_3 and UN first reported by them. The region between UN and U_2N_3 consists of two phases, whilst the region between U_2N_3 and UN_2 is a homogeneous solid solution in which the U_2N_3 structure changes with increasing nitrogen content into the UN_2 structure.

Uranium nitride, UN, has a face-centred cubic lattice with $a = 4{\cdot}880$ A. and calculated density of $\rho = 14{\cdot}32$ g./c.c.; it is strictly isomorphous with uranium carbide. An interesting observation is that the solubility of uranium or nitrogen in uranium nitride is extremely small. Uranium nitride (i.e. UN) does not have the wide range of composition associated with most other interstitial compounds; its empirical formula is exactly UN. Uranium sesquinitride, U_2N_3, has a body-centred cubic lattice with $a = 10{\cdot}678 \pm 0{\cdot}005$ A., and a calculated density of $\rho = 11{\cdot}24$ g./c.c.; This structure is isomorphous with that of manganese sesquioxide. Uranium sesquinitride forms solid solutions with nitrogen at least up to $UN_{1\cdot75}$; this progress toward UN_2 is attended by a change in structure from a distorted type of calcium fluoride lattice to that of UN_2, which is of the fluorite type. It seems that at high pressure U_2N_3 disproportionates into UN and UN_2. Uranium dinitride, UN_2, which can be formed only at high pressure (120 atm.) has a face-centred cubic structure of the fluorite type with $a = 5{\cdot}31$ A.

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The existence of only three nitrides having the compositions given by Rundle *et al.* has been confirmed by Vaughan,[42] but the *X*-ray pattern he obtained for U_2N_3 does not agree with that obtained by Rundle; Vaughan found his structure to be isomorphous with that of Th_2N_3 and he suggests that U_2N_3 is polymorphic, having two forms.

By heating uranium, or preferably the hydride formed from the metal and hydrogen at 200–400°C., with excess of nitrogen or ammonia at the same temperature a nitride is produced with a weight gain corresponding to $UN_{1\cdot5-1\cdot75}$.[43, 44] Calcining at 1400°C. reduces the nitrogen content to slightly under that of the nitride UN, but the *X*-ray pattern indicates a simple sodium chloride lattice and a single pure phase (cf. Rundle[41]).

Uranium mononitride has also been prepared[45] by the reaction between either nitrogen or ammonia and uranium shavings at 300°C., ammonia giving a more finely divided product. The melting point of various samples in an atmosphere of ammonia ranged from 2575° to 2710°C.

Small uranium nitride crucibles, prepared by pressing UN powder at between 50,000 and 60,000 lb./sq. in. and firing at between 2000° and 2100°C., had a density of approximately 12 g./c.c., indicating a porosity of 16%, if 14·32 g./c.c. is taken as the calculated density of the pure nitride.

In a review Hoekstra and Katz[46] state that the best method for preparing pure uranium nitride, UN, is by the reaction of uranium hydride with the calculated quantity of ammonia at 600°C. or with nitrogen at 350°C., oxygen being completely excluded.

A possible method of removing oxygen from nitrogen by passing the gas over $UN_{1\cdot5-1\cdot75}$ at 500–600°C. has been proposed,[47–49] the uranium nitride being first prepared by passing nitrogen or ammonia over uranium turnings at about 800°C.

The nitrides of uranium are easily oxidized in air, sparingly soluble in acids, inert to aqueous alkali solutions, but decomposed by molten alkali.[46] The chemistry of uranium nitrides is discussed also by Jensen and Mundy[50] and by Dounce *et al.*[51]

PROPERTIES OF URANIUM MONONITRIDE

Certain properties of the uranium nitrides have been reported[52] in a survey by the U.S. Atomic Energy Commission. The mononitride is one of the most stable nitrides, only ZnN, HgN and ThN being more stable. It melts at 2900°C. and vaporizes only by dissociation into uranium and nitrogen; the resulting vapour pressure at 2000°K. is calculated to be about 10^{-8} atm. and at 2500°K. between 10^{-4} and 10^{-5} atm. The heat of formation at 298°K. is $\Delta H_{298} = -80$ kcal./mole and the value of the thermodynamic function:

$$\frac{(\Delta F - \Delta H_{298})}{T}$$

at 298°K. is 17 e.u. (equivalent to $-\Delta S$ of formation). At 298°K. the entropy of UN is 18 e.u. Similarly for U_2N_3 $\Delta H_{298} = -213$ kcal./mole, $\Delta S_{298} = 64$ e.u. and $S_{298} = 29$ e.u. For $UN_{1\cdot65}$, a solid solution of U_2N_3 in UN_2, $\Delta H_{298} = -68\cdot5$ kcal./mole, $\Delta S_{298} = 22$ e.u. and $S_{298} = 8$ e.u.

The rate of reaction of nitrogen with uranium has been studied[53] by volumetric measurements in the temperature range 550–900°C. at atmospheric pressure. The reactions follow a parabolic rate law with some deviations initially and also after the period of parabolic reaction (see Figs. 32, 33). Fig. 34 shows the variation of the parabolic rate constant with temperature. Surface reaction products formed in the temperature range 550–750°C. were identified by *X*-ray diffraction studies as principally UN_2 with slight evidence of U_2N_3 in some cases: between 775° and 900°C. the three nitrides, UN, U_2N_3 and UN_2, were found in the surface reaction product. The parabolic rate constant for the reaction between 550° and 750°C. is

$$k = 202\ e^{-25{,}500/RT}$$

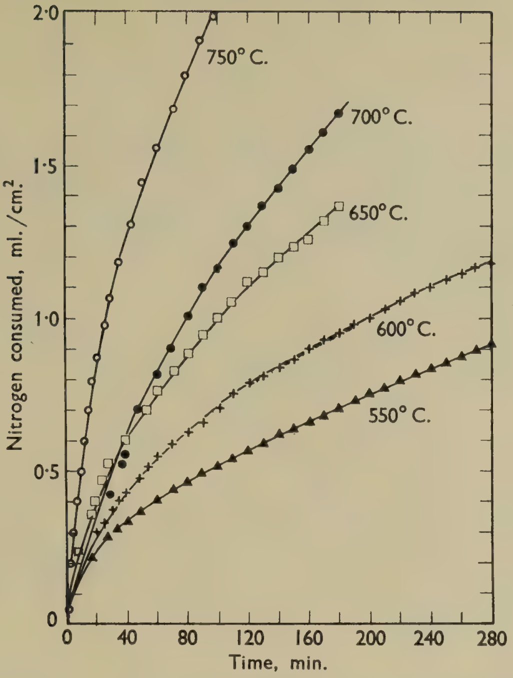

FIG. 32.—The uranium–nitrogen reaction at 550–750°C.

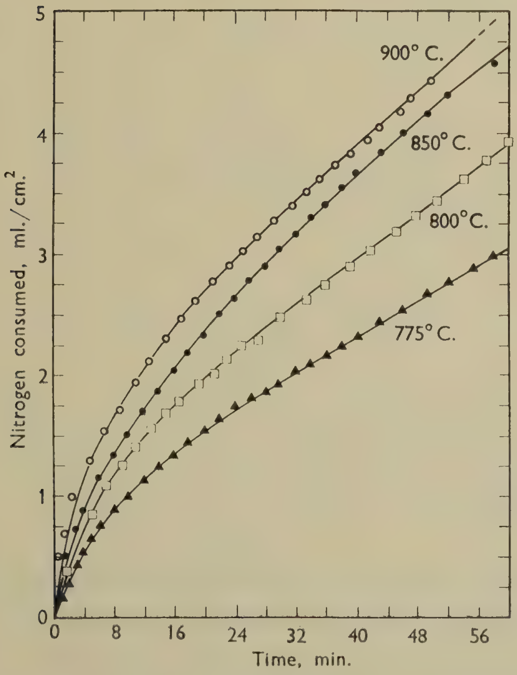

FIG. 33.—Uranium–nitrogen reaction at 775–900°C.

the activation energy being 25,500 g.-cal./mole: between 775° and 900°C. the constant is

$$k = 3{\cdot}95\ e^{-15,100/RT}$$

and the energy of activation 15,100 g.-cal./mole.

In studies of the decomposition pressure of nitrides, Lorenz and Woolcock[54] found that the nitrogen pressure in equilibrium with the system U–N increases with increasing nitrogen content; at 1280° and 1480°C., p ranging from 2·5 mm. to 656 mm. at 1280°C. as the absorbed nitrogen increases from 0·0992 to 0·9230 g.-atom per g. atom of uranium. At the higher temperature a smaller nitrogen content was obtained at a given pressure than at 1280°C.

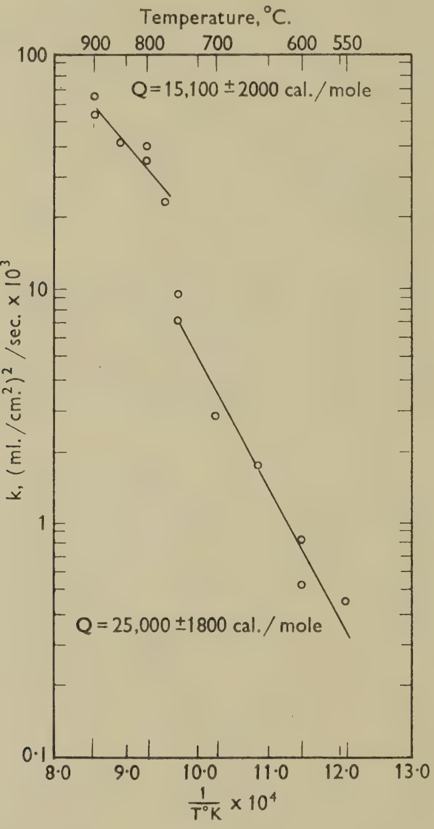

FIG. 34.—Uranium–nitrogen reaction: variation of parabolic rate constant with temperature

Uranium mononitride is found not to be a super-conductor down to a temperature of about 1·2°K.[55]

Nitrides of Protoactinium, Neptunium, Plutonium and Polonium

Protoactinium nitride, PaN_2, has probably been prepared by the action of ammonia on the chlorides '$PaCl_5$' or $PaCl_4$ at 150°C., although according to Elson[56] it is possible that oxygen atoms are present in the crystal. The resulting light-yellow solid appears to be isostructural with UN_2.

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Neptunium nitride, NpN, can be prepared by causing neptunium hydride, NpH_3, to react with ammonia at 750–775°C.[57] Attempts to prepare this nitride by the reaction of ammonia with neptunium tetrachloride were unsuccessful. Neptunium nitride has predominantly metallic characteristics and possesses a rock salt structure with lattice parameter $a = 4{\cdot}887$ kX. and density 14·1 g./c.c.[58]: it is isomorphous with uranium nitride, UN, and plutonium nitride, PuN. It is a black substance, insoluble in water but soluble in hydrochloric and nitric acids.

Brown *et al.*[59] found that plutonium metal reacts with nitrogen to a small extent above 250°C.; the reaction is superficial and prolonged heating to 1000°C. does not bring about complete conversion to the nitride. Plutonium nitride can be prepared[60] by the reaction of the metal with dry ammonia at 1000°C., or of the trichloride, $PuCl_3$, with dry ammonia at 900°C., or of powdered plutonium hydride with dry ammonia above 280°C. Pure plutonium nitride is black, becoming light brown after a few days owing to hydrolysis. Like the metal it is dense, hard and brittle. It is attacked by mineral acids with the formation of an insoluble hydrated oxide, the nitrogen being converted quantitatively into ammonium salts. Its outstanding property is its ease of hydrolysis by warm, moist air.

Its heat of formation is estimated to be approximately 95 kcal./mole.[4]

It is a typical interstitial nitride and has a rock-salt structure, isomorphous with PuO, with $a = 4{\cdot}906$ A., $c = 4{\cdot}905 \pm 0{\cdot}002$ A.[3, 4] The density is 14·2 g./c.c.

Bagnall[60] states that since polonium metal distils unchanged in nitrogen the nitride cannot be formed from its elements. A black compound is formed by heating ammonium hexabromopolonite at 200°C.: this can be detonated, indicating that an explosive nitride analogous to Te_3N_4 is possibly formed under these conditions.

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NITRIDES OF GROUP VII METALS

Manganese Nitrides

PREPARATION

In a study of the absorption of nitrogen by manganese at 760 mm. pressure and 610°C., the formation of the compound Mn_3N_2 was indicated.[1]

Ochsenfeld[10] observed that when manganese is heated rapidly in nitrogen, a rapid absorption of up to 11 atom-% occurs in the neighbourhood of 1100°C., accompanied by the appearance of ferromagnetic properties and an increase in the lattice parameter from 3·772 to 3·857 A. On raising the temperature to about 1300°C., the nitrogen is given up and the ferromagnetism disappears; it was therefore assumed that the lattice of manganese is of the γ type. The γ phase is face-centred tetragonal and on cooling below 500°C. decomposes into two forms, one cubic and the other close-packed hexagonal.

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Schenck and Kortengräber[2] from their equilibrium isotherms for manganese and nitrogen infer the formation of a nitrogen-poor face-centred cubic phase corresponding to the ϵ phase of Hägg (see below) and also a nitrogen-rich hexagonal phase which is identical with Hägg's ζ phase.

Neumann *et al.*,[3] on heating manganese in nitrogen at 500–1000°C. and 10–25 atm. pressure, obtained a compound corresponding closely to Mn_5N_2, which is probably the lower limit of the 'Mn_2N' phase.

Guillaud and Wyart[4] prepared manganese nitrides by heating powdered manganese in high-pressure nitrogen at 700–800°C. for 1000 hours; a maximum of 32% of nitrogen was incorporated at 740° and 200 atm. pressure.

Zwicker,[5] after nitriding manganese with ammonia at 850°C. for 15 hours, found a greyish brown non-ferromagnetic phase possessing a hexagonal lattice (with $a = 2{\cdot}778$ A, $c/a = 1{\cdot}62$) and a greyish blue ferromagnetic phase, face-centred cubic (Mn_4N), with $a = 3{\cdot}865$ A.; faint superstructure lines were also observed. After nitriding with ammonia at 730°C. for 2 hours the manganese was not homogeneous and showed various zones with α-manganese at the centre, then β-manganese, Mn_4N and finally Mn_2N on the outside. The richest nitrogen-containing substance was obtained after nitriding at 850°C. for 15 hours and then at 525°C. for 15 hours. This contained 38·8 atom-% of nitrogen (14% by weight) and showed a tetragonal structure with $a = 4{\cdot}205$ A. and $c/a = 0{\cdot}98$. A compact sample prepared in the same way had a composition of 30 atom-% of nitrogen and a hexagonal lattice. When heated in nitrogen at 700°C. this sample showed no composition changes. When heated to 1000°C. and water-quenched the sample changed from the hexagonal form to a paramagnetic face-centred cubic phase, $a = 3{\cdot}855$ A., containing 20 atom-% of nitrogen.

For the investigation of the lower nitrogen-content region the metal was nitrided in air at 950–1150°C. At 950°C. the metal becomes ductile in 1 hour, whilst at 1150°C. this requires only 25 minutes. A ductile sample hammered into wire and heated at 750°C. for 3 hours in an evacuated tube and then water-quenched showed tetragonal γ-manganese, with $a = 3{\cdot}762$ A. and $c/a = 0{\cdot}972$ as well as cubic β-manganese with $a = 6{\cdot}318$ A. Another sample quenched from 1150°C. showed tetragonal γ-manganese with $a = 3{\cdot}75$ A. and $c/a = 0{\cdot}964$.

THE MANGANESE–NITROGEN SYSTEM

On the basis of the above work Zwicker prepared a phase diagram which has been superseded by the same author[6] basing his diagram, Fig. 35, on his own work and a literature survey, but he disregarded the results of Duparc *et al.*[7, 8] as they were not obtained under equilibrium conditions.

The three intermediate phases ϵ-Mn_4N, ζ-Mn_2N, η-Mn_3N_2 and a fourth metallic phase, stable only above 500°C., were first identified by Hägg[9] by the method of *X*-ray analysis.

The ϵ phase (Mn_4N) has a small range of homogeneity.[9] The unit cell is face-centred cubic with $a = 3{\cdot}865$ A.,[5] or 3·874 A.[2] Faint super-lattice lines corresponding to (100) and (110) diffractions were detected. It is strongly ferromagnetic with a Curie point at 465°C. and it is isostructural with Fe_4N.

The ζ-phase Mn_2N is a hexagonal close-packed structure with a range of homogeneity up to 12 wt.-% of nitrogen at 400°C. The lattice constants[9] increase with increasing nitrogen content from $a = 2{\cdot}779$ kX., $c = 4{\cdot}529$ kX. and $c/a = 1{\cdot}630$ at 27·2 atom-% of nitrogen to $a = 2{\cdot}834$ kX., $c = 4{\cdot}537$ kX., $c/a = 1{\cdot}601$ at 35·0 atom-% of nitrogen. Zwicker gave a single value of $a = 2{\cdot}77$ A., $c/a = 1{\cdot}62$, whilst Schenck and Kortengräber[2] gave $a = 2{\cdot}787$ A., $c/a = 1{\cdot}61$.

The η phase (Mn_3N_2), which is non-magnetic, has a range of homogeneity from 13·5 to 14 wt.-% of nitrogen: it has a tetragonal unit cell, the lattice parameters of which are $a = 4{\cdot}20$ kX., $c = 4{\cdot}039$ kX., $c/a = 0{\cdot}9612$ at 37·8 atom-% of nitrogen and $a = 4{\cdot}215$ kX., $c = 4{\cdot}137$ kX., $c/a = 0{\cdot}9815$ at 38·8 atom-% of nitrogen.[9] Zwicker[5] gave the values $a = 4{\cdot}205$ A., $c/a = 0{\cdot}98$.

More recently (1957) Juza and co-workers[11] reinvestigated some aspects of this system by *X*-ray, thermo-magnetic and magnetization-intensity measurements on samples prepared by causing manganese and nitrogen to react at 1000°, 800°, 600° and 400°C. Besides finding different phase limits (see Fig. 36) at these temperatures, evidence was obtained of an additional phase which contains 9·8 to 15 atom-% of nitrogen in the 1000°C. preparations: it has the same lattice structure as the ϵ phase, but less nitrogen. Figs. 37, 38, 39 and 40 give the phase lattice constants and Curie temperature for the 1000°, 800°, 600° and 400°C. preparations, whilst Fig. 41 gives the lower phase limits and the lattice constants of the ζ phase; this lattice diagram also includes the values of Hägg.

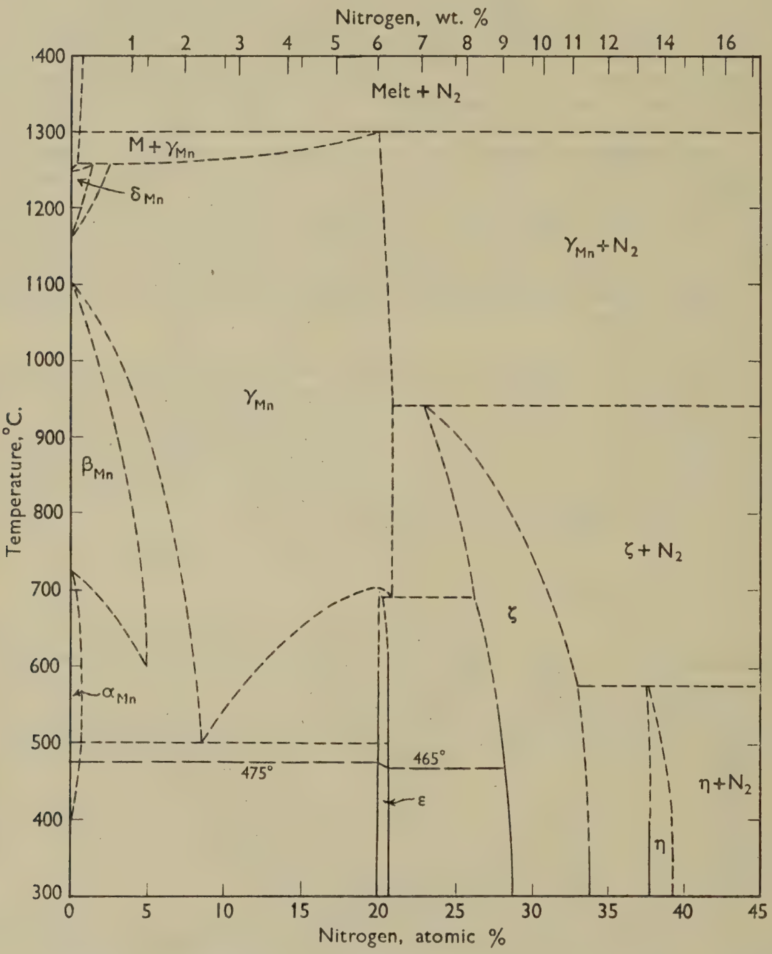

FIG. 35.—Manganese–nitrogen tentative phase diagram. (By permission from 'Constitution of Binary Alloys' by Hansen & Anderko, Copyright 1958, McGraw-Hill Book Co.)

Nishiyama[12] found that when electrolytic manganese is treated at 600°C. for 3 hours with ammonia, the Debye–Scherrer diagram shows two face-centred ($\eta_1 + \eta_2$) tetragonal and one face-centred (θ) cubic phase; the lattice constants are: (η_1) $a = 4{\cdot}211$ A., $c = 4{\cdot}130$ A., (η_2) $a = 4{\cdot}154$ A., $c = 4{\cdot}037$ A., (θ) $a = 4{\cdot}435$ A.; the nitrogen content of the θ phase was estimated to be about 21 wt.-%.

The relationship between nitrogen content and magnetic properties of manganese

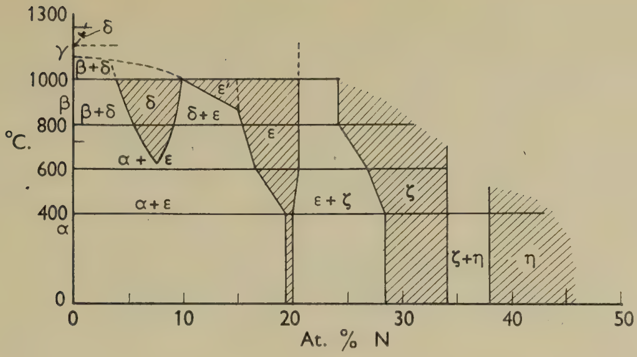

FIG. 36.—Partial phase diagram of the manganese–nitrogen system

has received some attention,[4, 11, 14–18] Guillaud and Wyart found that for ferromagnetic nitrides the distance between adjacent manganese atoms is

$$2{\cdot}702\ \text{A.} \leqslant d \leqslant 2{\cdot}727\ \text{A.}$$

Pearson and Ende in a thermodynamic review[19] state that there is little reliable information on the formation of manganese nitrides. The reader is also referred to a review of this system presented by Sully.[13]

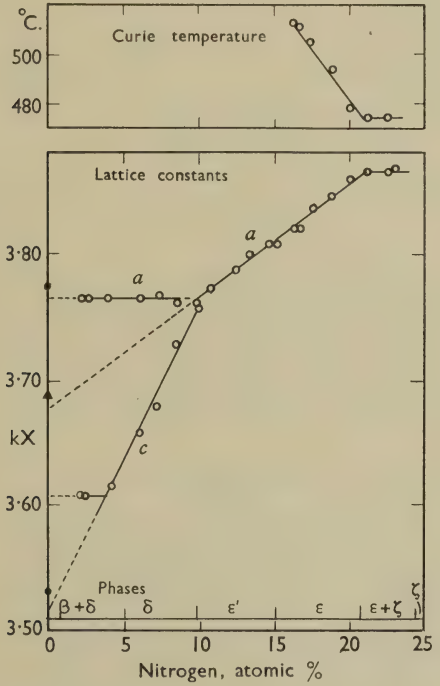

FIG. 37.—Phases, lattice constants and Curie temperatures for 1000°C. preparations

- ● Lattice constants of tetragonal γ-manganese
- ○ Lattice constants of cubic γ-manganese, extrapolated from 20°C.

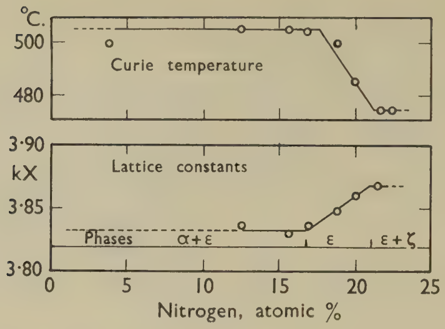

FIG. 38.—Phases, lattice constants and Curie temperatures for 600°C. preparations

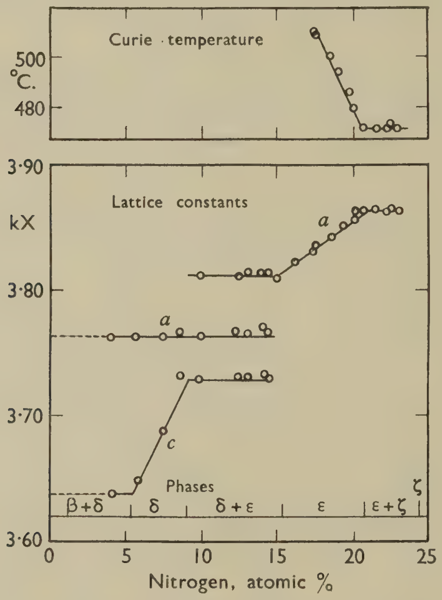

FIG. 39.—Phases, lattice constants and Curie temperatures for 800°C. preparations

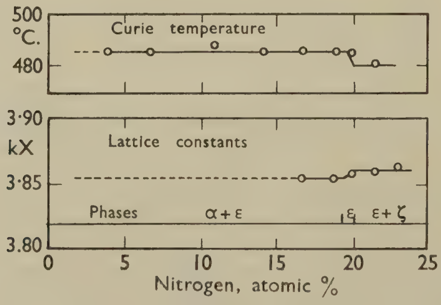

FIG. 40.—Phases, lattice constants and Curie temperatures for 400°C. preparations

Neumann *et al.*,[3] from measurements of the heat of solution of the nitride designated 'Mn_5N_2' in sulphuric acid, estimate that the heat of formation is $\Delta H = -59{\cdot}34$ kcal./mole; by direct nitriding $\Delta H = -57{\cdot}18$ kcal. (constant volume) and by burning in oxygen $\Delta H = -62{\cdot}4$ kcal./mole. Kelley[20] states that the best figure for ΔH (constant pressure) is $\Delta H = -57{\cdot}77$ kcal./mole (recalculated from the direct nitriding value) and hence $\Delta H^\circ_{298\cdot1} = -46{\cdot}920$ kcal./mole.

Satô[21] from dissociation pressure measurements and specific heat equations[22] calculates $\Delta H = -57{\cdot}0$ kcal./mole for 'Mn_5N_2' and $\Delta H = -79{\cdot}8$ kcal./mole for Mn_4N. The molar heat capacities are given by the following equations:

$$C_p = 22{\cdot}23 + 2{\cdot}2 \times 10^{-2}T + 9{\cdot}625 \times 10^{-7}T^2 \text{ for } Mn_3N_2$$
$$C_p = 33{\cdot}02 + 3{\cdot}096 \times 10^{-2}T + 4{\cdot}93 \times 10^{-6}T^2 \text{ for } Mn_5N_2$$
$$C_p = 46{\cdot}98 + 4{\cdot}238 \times 10^{-2}T + 1{\cdot}767 \times 10^{-5}T^2 \text{ for } Mn_4N$$

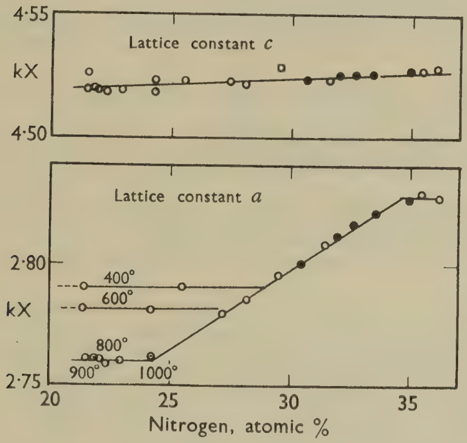

FIG. 41.—Lower phase limits of the ζ phase
● Hägg's results
○ Juza's results

Maier[23] has criticized Neumann's work on the ground that his measurements were made on a mixture of Mn_3N_2 in manganese. Pearson,[19] however, considers this criticism unjustified and that in fact Mn_5N_2 is really the lower limit of the Mn_2N phase; Kelley,[20] however, agrees with Maier. It seems clear that the manganese–nitrogen system, as to phase relationships, thermodynamic data, etc., requires further investigation.

Rhenium Nitride

A nitride of rhenium has been prepared by Hahn[24] by the action of ammonia on ammonium rhenate or rhenium trichloride at 300–350°C. It is an interstitial nitride with a maximum nitrogen content corresponding to $ReN_{0\cdot43}$ and crystallizes in a face-centred cubic lattice, 4 molecules to the unit cell, with lattice parameter $a = 3{\cdot}92$ A., the N atoms occupying the octahedral spaces.

Rhenium nitride is thermally unstable. After prolonged heating in vacuo it begins to decompose at about 280°C., which explains the difficulty in preparing it and the impossibility of obtaining it from the elements.

It is a black substance which oxidizes to perrhenic acid, $HReO_4$, on standing for some time in moist air; under the same conditions the metal is pyrophoric. Air-free water is without action, but in aqueous alkalis and in the presence of oxygen it dissolves to form perrhenates. It dissolves slowly in dilute and rapidly in concentrated nitric acid. Hot concentrated sulphuric acid attacks it slowly whilst hydrofluoric and hydrochloric acids are without action. Chlorine and oxygen have the same effect on the nitride as on the metal. Hydrogen reduces the nitride at 250°C. The heat of formation is approximately zero.

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NITRIDES OF GROUP VIII METALS

Iron Nitrides

PREPARATION

The general method of preparing iron nitrides is as follows.[1, 2, 9–13, 76] Anhydrous ammonia–hydrogen mixtures after purification are passed over fine iron powder (99·9% pure) at atmospheric pressure, at various temperatures and at sufficiently high rates of flow to ensure only slight dissociation of ammonia. At 450°C., for example, the γ' nitride (see below for phase diagram) is formed, the nitrogen content of which depends on the ratio of ammonia to hydrogen. Above 450°C. with pure ammonia, ϵ-phase nitrides with not more than 11·0% of nitrogen are formed, but at temperatures not exceeding 450°C., ζ nitrides with 11·1–11·3% of nitrogen are obtained.

At temperatures ranging from 700–750°C.[3] nitrogen–austenite (γ phase) and nitrogen–martensite can be obtained.

Addition of small quantities of ferrous sulphide retards considerably the transformation of Fe_2N to Fe_4N at 400–600°C.[77]

The ϵ nitride or iron containing 5·7–5·9 wt.-% of nitrogen is prepared also by heating 15% manganese–iron alloy powder in an ammonia–hydrogen gas mixture and then quenching,[2] the function of the manganese being to stablilize the nitrides on quenching. Treatment of ferrous bromide with potassium in liquid ammonia at −33·5°C. yields *inter alia* 'Fe_3N'.[78] At 430°C. Fe_2N is obtained in the reaction of ferric oxide with ammonia.[92]

The preparation of the following complex nitrides is also reported:

$Li_2O,4Fe_3N,4Fe_2N$, $2Li_2O,Fe_2O_3,6Fe_3N$, $(Li_2O,Fe_2O_3)_3,2Fe_3N$, $3Cu,2Fe_3N$, Cu,Fe_3N, $3Cu,4Fe_3N$, $Cu,2Fe_3N$, $3Cu,8Fe_3N$, $3Cu,10Fe_3N$.[92]

It is now realized that nitrogen is important in ferrous physical metallurgy in such phenomena as strain ageing and temper embrittlement. It is a powerful austenite stabilizer and may be a useful alloying element in stainless steels. It has been found also that the hardenability of steels is increased by presence of nitrogen. An understanding of the part played by nitrogen in the metallurgy of iron depends on knowledge of the phase relationships.

When an arc is formed between iron poles in an atmosphere of nitrogen, a compound, 'Fe_4N_2', is formed in the metal–vapour zone.[42]

In an investigation of the nitriding of iron with ammonia–hydrogen mixtures at 375–500°C. and atmospheric pressure, Krichevsky and Khazanova[45] observed that the reaction stopped almost completely as a limiting nitrogen content in the iron is approached, the final nitrogen content increasing with increase in temperature or ammonia concentration. They concluded that nitriding is the result of two opposing reactions:

$$2NH_3 + 2xFe \rightarrow 2Fe_xN + 3H_2; \qquad 2Fe_xN \rightarrow 2xFe + N_2$$

The first reaction is limited by the rate of diffusion of nitrogen through the iron and iron nitrides, and slows down as nitride formation increases until equilibrium between the two reactions is attained.

In an investigation of the action of gaseous nitrogen on iron vapour (at 1200–1500°K., 0·1 mm. Hg), the results were negative; iron atoms do not react with nitrogen molecules.

THE IRON–NITROGEN SYSTEM

A variety of phase diagrams for the iron–nitrogen system recorded in the literature up to 1930[5–15, 74] (Mellor, VIII, 134) differ significantly from one another.

In a critical discussion of the experimental methods (which include thermal analysis, microscopical examination, *X*-ray diffraction, magnetic measurements, dilatometric analysis and anelastic experiments) Paranjpe *et al.*[4] point out that thermal analysis has a low order of accuracy in determining changes in the solid state, and that this accuracy is further decreased for iron–nitrogen alloys since composition changes occur during heating and cooling unless extreme care is taken to use the correct atmosphere. The same criticism applies to the dilatometric method because composition changes may occur during heating and cooling. Metallographic methods are of little value in that the production of iron–nitrogen alloys of sufficient size is difficult. The determination of lattice parameters for phase boundary estimations can be made satisfactorily if cooling is fast enough to prevent structural changes. In view of these limitations to the above-mentioned techniques, Paranjpe *et al.* determined the phase diagram of the iron–nitrogen system partly by *X*-ray diffraction and partly by a new technique, viz., the controlled nitriding of iron powders in ammonia–hydrogen mixtures. Their results are given in Fig. 42. At about the same time, Jack[2, 3] also published a phase-diagram (see Fig. 43) based on Dijkstra's[16] results for the α solid solution limits, on the work of Lehrer[7] for the γ, γ' and ϵ phase relationships and on his own observations of the ζ phase limits and of many of the phase boundaries. It differs slightly from the diagram of Paranjpe, but only in certain phase composition limits. According to Paranjpe the α phase (nitrogen ferrite) contains small amounts of nitrogen in solution reaching a maximum solubility of 0·10% at the eutectoid temperature of 590°C. This seems to be in reasonable agreement with other solubility data reported more recently (see below). The composition limits for the γ phase (nitrogen austenite)—maximum solubility 2·80% of nitrogen at 650°C.—are in good agreement with the findings of Lehrer and of Eisenhut and Kaupp.[8] The γ' phase exists over a very limited range of composition, the homogeneity limits according to Paranjpe being 5·47 to 5·80% of

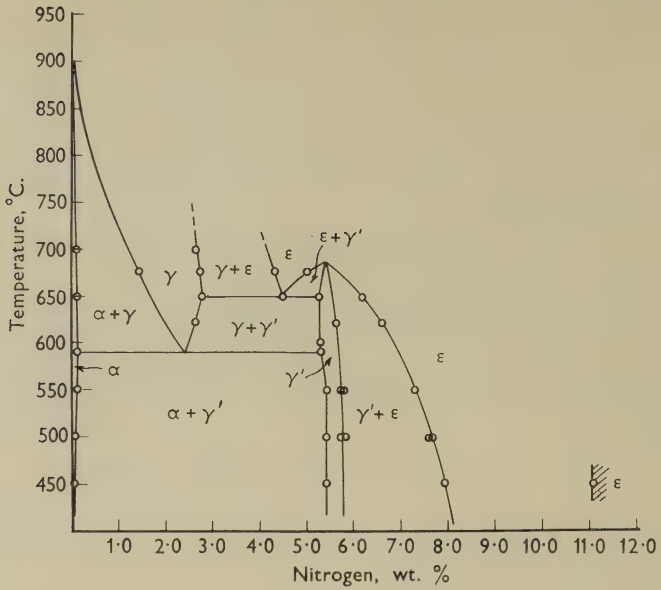


Fig. 42.—Iron–nitrogen phase diagram (Paranjpe *et al.*, 1950)

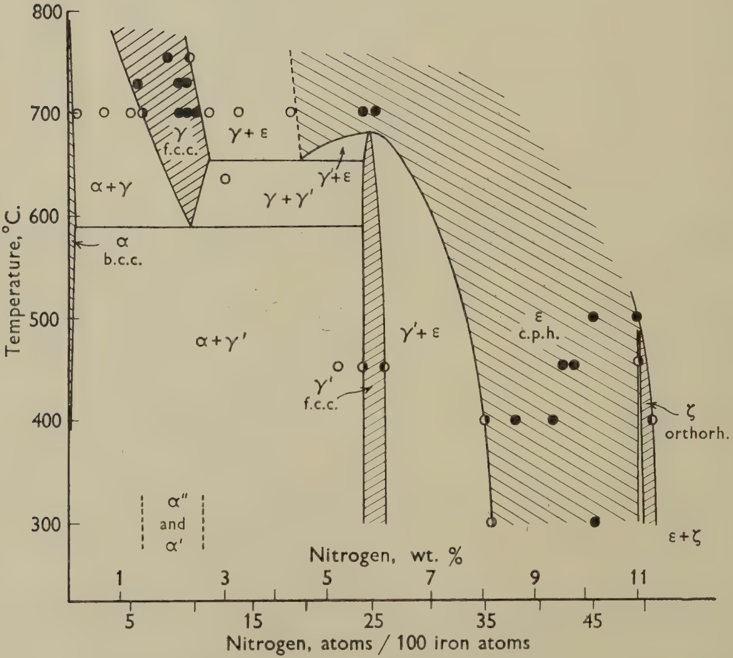
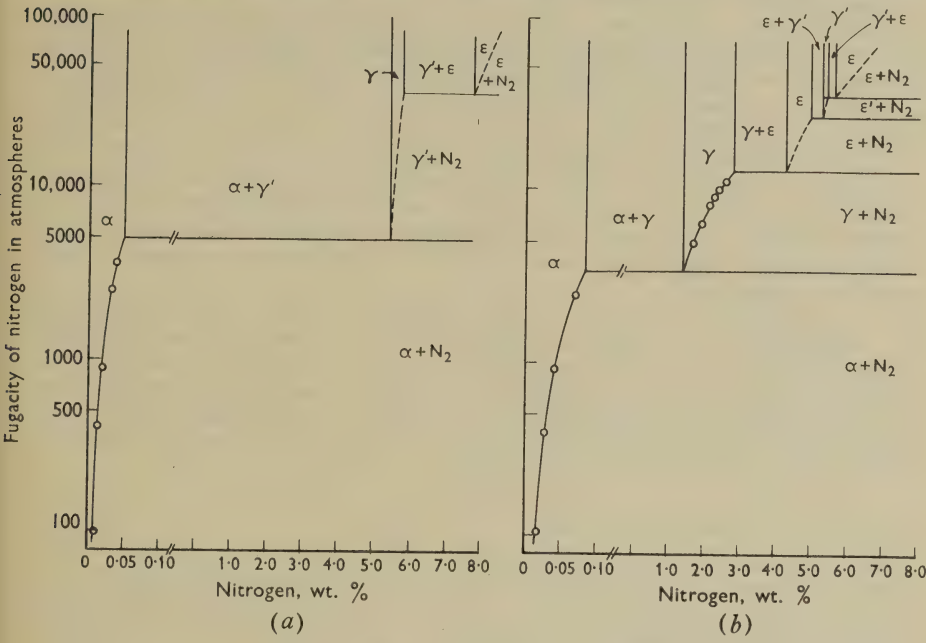


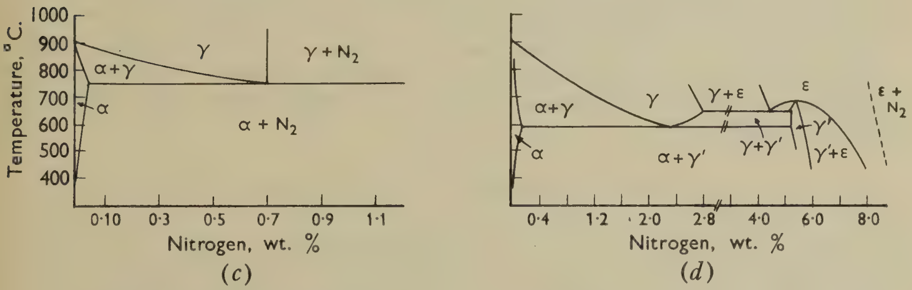
Fig. 43.—Iron–nitrogen phase diagram (Jack, 1951)

nitrogen. A slightly different homogeneity range has been found by Jack[1]: at 450°C. 5·7 to 6·1% of nitrogen which includes Fe_4N (5·90% of nitrogen). This agrees with the earlier work of Hägg[9–13] and of Eisenhut and Kaupp.[8] An important point to note is that Paranjpe's range for this phase is outside the composition corresponding to Fe_4N.

The ϵ phase has a wide range of homogeneity, viz., 4·35 to 11·0% of nitrogen.[4] The ζ phase (Fe_2N) originally discovered by Hägg[12] has, according to Paranjpe, a lower homogeneity limit of 11·1% of nitrogen at 450°C., which is also in good agreement with Jack's work.[3] Attempts to produce the ζ phase at 475° and 500°C. were unsuccessful.



Isothermal section at 500°C. Isothermal section at 675°C.



Isofugacity section at 1000 atm. Isofugacity section at 50,000 atm.

FIG. 44.—Effect of pressure on the iron–nitrogen phases

Dijkstra[16] observed that the first-formed precipitate in the low-temperature heat-treatment of α-iron–nitrogen solid solutions is not Fe_4N, but another nitride. Wert[17] also has noticed the formation of what he considered a new type of nitride under the same conditions. Jack[18] observed that there are broad analogies between the mechanisms of martensite tempering in the iron–carbon and iron–nitrogen systems and he found that in the decomposition of nitrogen-martensite (α′) to ferrite and

Fe_4N (γ'phase) there is a transition phase, relatively stable, which he calls the α'' iron nitride containing 1·5–3·0 wt.-% of nitrogen; this nitride has the empirical formula $Fe_{16}N_2(\equiv Fe_8N)$, and is the nitride identified by Dijkstra and by Wert.

Hopkins and Tipler[75] found that addition of 0·01% of nitrogen to high purity iron caused the appearance of intergranular brittleness that was sensitive to heat-treatment. The nitride '$Fe_{16}N_2$' was precipitated in these alloys by slow cooling in a furnace to room temperature, although occasional needles of Fe_4N were also seen. Heating at 200° or 250°C. for prolonged periods resulted in the disappearance of $Fe_{16}N_2$ and the formation of Fe_4N.

Jack[18] points out that when steel is nitrided under conditions such that nitrogen austenite is formed, the austenite and martensite transformation occurs on cooling, the properties of the product being similar to those of a carburized material after quenching. It is usual to temper martensite carbon-steels subsequently; maximum hardness is associated with the coherent precipitation of the ϵ-iron carbide transition phase. In the case of nitrogen steels the formation of the α'' phase during tempering may result in even greater hardness with equally valuable characteristic properties. Furthermore since the α'' phase is also the iron nitride precipitated when nitrogen ferrite is heat treated at low temperature, it is probable that the brittleness which develops by ageing steels which contain small amounts of nitrogen is associated with this phase.

The phase diagrams presented in Figs. 42 and 43 represent only two variables, viz., temperature and concentration. For a metal–gas system a three-dimensional diagram is necessary, the third variable being pressure. The effect of pressure on the iron–nitrogen phases has been investigated by several workers[57–60]; the most detailed and important of these investigations is that of Paranjpe and Cohen.[57] Four sections (two isothermal and two isofugacity) through the temperature–fugacity–concentration diagram are given in Fig. 44.

SOLUBILITY OF NITROGEN IN α-IRON

Much work has been done on the solubility of nitrogen in α-iron.[4–6, 8–14, 16, 18–30] Fast and Verrijp[19] point out that it is necessary to distinguish between the case where the metal is in equilibrium with an iron nitride Fe_4N or 'Fe_8N' and the case where only gaseous nitrogen, N_2, is present as a second phase. For the solubility of nitrogen in α-iron in equilibrium with Fe_4N, widely different results have been reported by several investigators. Fast[19] emphasizes that in measuring the solubility of nitrogen in α-iron in equilibrium with Fe_4N, the presence of finely divided Fe_4N or 'Fe_8N' may result in values that are too large, while the presence of lattice faults, especially dislocations, may produce values which are too small. These data, obtained by measurements of the internal friction of nitrogen-containing α-iron, are given in Table VI.

Table VI.—Solubility of Nitrogen in α-iron

Temperature, °C.	In Equilibrium with		
	Fe_8N wt.-%N	Fe_4N wt.-% N.	Nitrogen (1 atm.) wt.-% N
20	$1{\cdot}4\times10^{-5}$		
100	$5{\cdot}2\times10^{-4}$		
200	$8{\cdot}8\times10^{-3}$		
300	$5{\cdot}5\times10^{-2}$	$8{\cdot}4\times10^{-3}$	
400	$2{\cdot}0\times10^{-1}$	$2{\cdot}5\times10^{-2}$	
500		$5{\cdot}5\times10^{-2}$	$9{\cdot}0\times10^{-4}$
585		$9{\cdot}5\times10^{-2}$	$1{\cdot}4\times10^{-3}$
700			$2{\cdot}4\times10^{-3}$
800			$3{\cdot}3\times10^{-3}$
900			$4{\cdot}5\times10^{-3}$

These data for Fe_4N conform to the equation:

$$q = 12{\cdot}3\,e^{-8300/RT}$$

where q is the solubility in wt.-% of nitrogen.

From this equation the maximum value at the eutectoid temperature for the solubility of nitrogen in α-iron in equilibrium with Fe_4N is 0·095 wt.-% of N_2. This agrees well with the value of 0·10% obtained by Paranjpe *et al.*,[4] and those of other workers.[26, 27, 29] The value of 0·14% obtained by Séférian[23–25] appears to be too high, and the extrapolated value obtained by Dijkstra,[16] 0·08%, seems to be too low. The most recent solubility results, given in Fig. 45, are those of Rawlings and Tambini[31]; the data of Dijkstra and Paranjpe are also shown for comparison. At the eutectoid temperature of 590°C., the solubility is 0·108%.

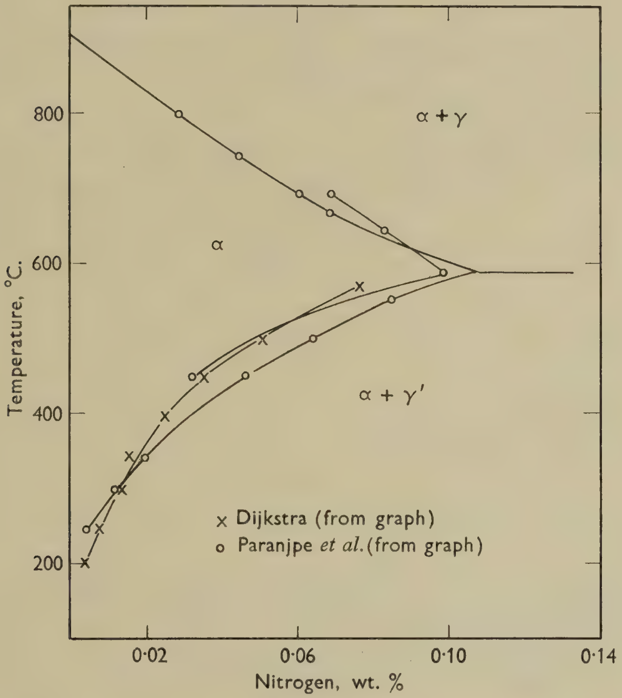


FIG. 45.—The α-phase boundaries of the iron–nitrogen system (Rawlings and Tambini)

The heat of solution of nitrogen in α-iron in equilibrium with Fe_4N is 8300 g.-cal. per g.-atom of nitrogen according to Fast.[19] Other workers report values of 5330 g.-cal.,[26] 6200 g.-cal.[27] and 7700 g.-cal.[16] Fast also calculates that the dissociation pressure of Fe_4N is in atm. given by the equation:

$$p_{N_2} = 1{\cdot}6 \times 10^4\,e^{-2200/RT}$$

Table V also gives the values obtained by Fast for the solubility (wt.-%) of nitrogen in α-iron in equilibrium with nitrogen at 1 atm. These values fit the equation:

$$q = 0{\cdot}098\,e^{-7200/RT}$$

From this equation Fast calculates that the values obtained for the solubility of nitrogen in δ-iron (stable between 1400°C. and 1540°C.) agree well with the figures determined by Sieverts and co-workers.[32, 33]

The results obtained by Fast[19] for the solubility of nitrogen (wt.-%) in α-iron in equilibrium with 'Fe_8N' are also given in Table V. These data fit the equation:

$$q = 3{\cdot}3 \times 10^2 \, e^{-9900/RT}$$

The solubility of nitrogen in iron at different temperatures for the α, γ, and δ allotropes in equilibrium with nitrogen at 1 atm. has been recently determined by Corney and Turkdogan.[29] Their results are given in Fig. 46, and a comparison made by these authors with some earlier work[32–34] shows very good agreement, though other work[35, 36] conflicts.

From experiments on the solubility of nitrogen in α-iron containing 2·83% Si Corney and Turkdogan[29] found that silicon reduces the solubility. Above 705°C. and for a nitrogen partial pressure of 1 atm., silicon nitride is not formed; at lower silicon concentrations this critical temperature is expected to be lower. Much recent work on the phases of the Fe–Si–N system[37] confirms that the presence of silicon causes a marked lowering of the solubility of nitrogen in iron and that the effect is greater at lower temperatures.[37]

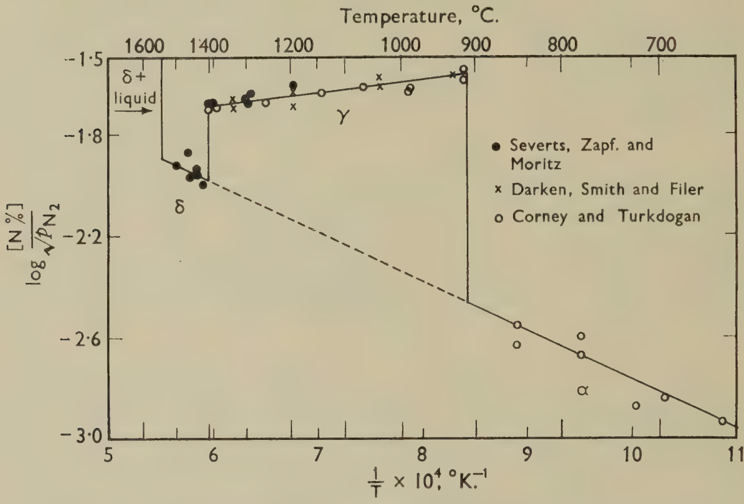


FIG. 46.—Solubility of nitrogen in α-, γ- and δ-iron in equilibrium with nitrogen at 1 atm.

Turkdogan *et al.* have shown that concentrations of up to 0·051% of vanadium in iron have no influence on the solubility of nitrogen in α-iron.

LATTICE STRUCTURES OF THE PHASES

The lattice parameter of the α phase is apparently identical with α-iron. As pointed out above, Paranjpe could not detect any appreciable change with increasing nitrogen content.

The γ phase—nitrogen austenite—possesses a face-centred cubic arrangement of the iron atoms and contains nitrogen in solution. It is isomorphic with the γ phase (austenite) of the Fe–C system. The nitrogen atoms of nitrogen austenite occupy up to a maximum of about 1 in 10 of the octahedral interstices of the face-centred cubic arrangement of iron atoms in a completely random manner.[3]

The lattice parameter increases with increasing nitrogen content,[8, 43] and the results of Jack[8] are given in Fig. 47, which also gives, for comparison, values of the austenite (γFe–C) lattice parameter. It will be seen from the graph that the linear variation of the γ-phase cell dimensions with nitrogen concentration (whether expressed in weight per cent, atoms per cent or percentage of interstices occupied), as observed by Eisenhut and Kaupp[8] and by Paranjpe *et al.*,[4] is not apparent in

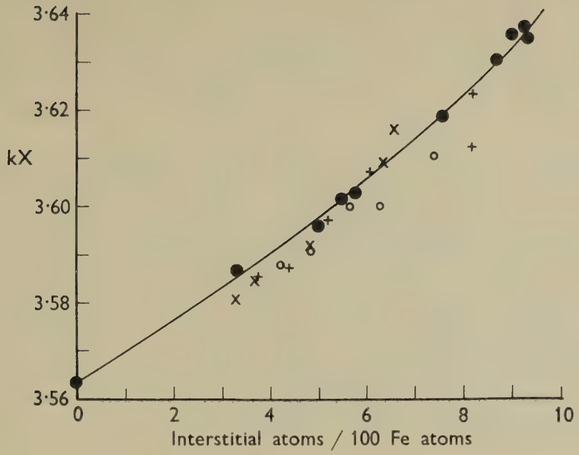


FIG. 47.—Unit cell dimensions for nitrogen–austenites and carbon–austenites
● N austenites (Jack)
C austenites
× Öhman
+ Honda & Nishiyama
○ Hägg

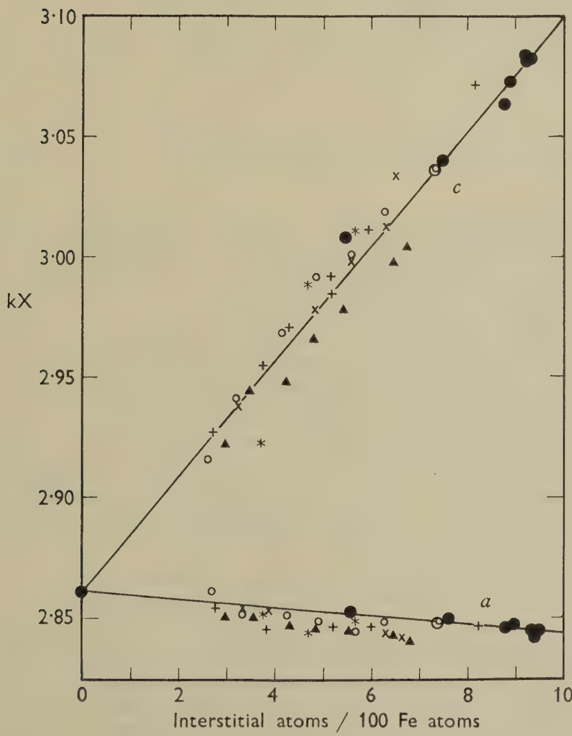


FIG. 48.—Unit cell dimensions of nitrogen–martensites and carbon–martensites
● Nitrogen martensite. Other points for carbon martensites

Jack's work. This author thinks there is no point in attempting to establish a relationship between unit cell dimensions and composition by weight; with an interstitial alloy compositions expressed in atoms-% have no particular significance. Jack considers that it is more logical to discuss dimensional changes in terms of the number of interstitial atoms for 100 metal atoms, since the number of available interstices is always equal to, or is a simple multiple of, the number of metal atoms in the crystal.

Nitrogen-martensite[3] has a body-centred tetragonal lattice and is isostructural with martensite (i.e., Fe–C-martensite). The lattice parameters '*a*' and '*c*' (which vary with the interstitial atom concentration) are shown in Fig. 48, which also shows the values observed for carbon-martensites by previous investigators. The structural components of the nitrogen-martensite lattice near its upper concentration limit are shown in Fig. 49. Jack[3] considers that the lattice may consist of octahedra of iron atoms joined together by shared edges and at most about 10% of these octahedra contain a nitrogen atom of radius $0{\cdot}7 \pm 0{\cdot}1$ A. at its centre and the lattice is thereby distorted. In nitrogen-martensite the displacements of iron atoms from the lattice points, owing to the occupation of certain octahedral interstices by nitrogen atoms, are considerably smaller than those calculated for carbon-martensite.

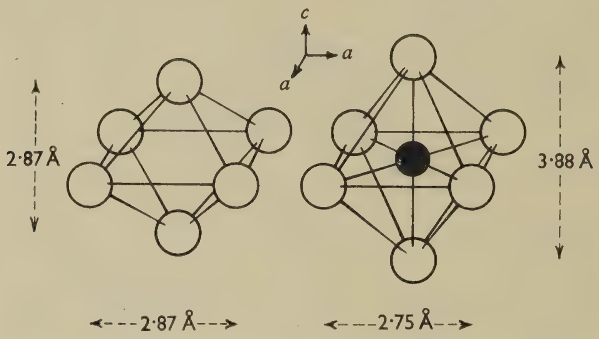


FIG. 49.—The structural components of nitrogen-martensite; ○ iron atom, ● nitrogen atom

The α″ structure according to Jack[18] is essentially a nitrogen-martensite in which the nitrogen atoms are completely ordered. The structural unit contains eight distorted and expanded body-centred tetragonal units of the original martensite structure. The contents of the unit cell, which has the dimensions $a = 5{\cdot}72$ A., $c = 6{\cdot}29$ A. $c/a = 1{\cdot}10$, are ideally $Fe_{16}N_2$. The iron atoms are displaced from sites occupied in the ferrite lattice by the presence of nitrogen atoms which occupy one twenty-fourth of the number of octahedral interstices in a completely ordered manner. Since the iron atom arrangement of Fe_4N (γ′) is face-centred cubic, the α″ structure ('Fe_8N') may be thought of as the Fe_4N structure in which the removal of alternate nitrogen atoms causes considerable distortion. For this reason α″ can be regarded as a transition structure between α′ and γ′. It is interesting to note that the volume of structure per metal atom for α″ (12·9 A.^{3}) is almost exactly midway between the corresponding values for body-centred cubic α-iron (12·0 A.^{3}) and face-centred cubic Fe_4N (13·7 A.^{3}).

According to Jack the γ′-phase ('Fe_4N') has a face-centred cubic structure, as previously suggested by Brill,[39, 40] in which the iron atoms are arranged in a face-centred cubic close-packed structure with nitrogen atoms equidistant from each other and occupying one fourth of the number of octahedral interstices in a completely ordered manner. The iron–nitrogen distance is 1·894 A., and '*a*' (unit cubic edge) is 3·787 A. for the nitride containing 6·1% of nitrogen.[1] Paranjpe[4] found that the lattice parameter varies from $3{\cdot}78_3$ A. at 5·29% of nitrogen to $3{\cdot}79_3$ A. at 5·71% of nitrogen. The structure is shown in Fig. 50.[39, 40]

The phase Fe_4N precipitated from a solid solution of nitrogen in α-iron takes the form of plates lying parallel to (210) planes in the α-iron matrix. A (112) plane in the Fe_4N structures lies parallel to a (210) plane in the α-iron matrix, presumably with the close-packed atoms in the two planes mutually parallel.[43, 44]

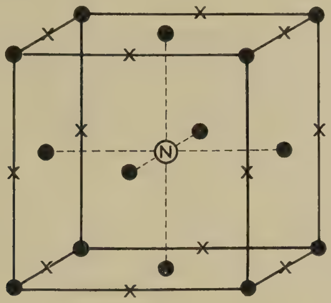


FIG. 50.—Structure of the γ' (Fe_4N) Fe–N phase
● iron atom
Ⓝ nitrogen atom
× unoccupied octahedral interstice

The ϵ-phase has a hexagonal close-packed structure and the unit cell dimensions are given in a comparative form by Jack[2] (see Fig. 51) who states that his results are in complete agreement with those of Brunauer *et al.*,[21] and Paranjpe.[4] Eisenhut and Kaupp[8] observe that the unit cell dimensions are a linear function of the nitrogen concentration, but this was not confirmed by Jack. Throughout the ϵ-phase range, the iron-atom arrangement is close-packed hexagonal. The arrangement of interstices is illustrated in Fig. 52. In agreement with the work of Hendricks and Kosting,[41] Jack proposes from *X*-ray analysis that the nitrogen atoms of the ϵ-nitrides occupy certain interstices in an ordered manner. For Fe_3N he considers that one-third of the interstices in each layer are filled in such a way that the six interstices nearest to a nitrogen atom in its own layer plane and the interstices directly above and below it in adjacent planes remain unoccupied, giving a sequence of nitrogen-atom layers ABAB.... ϵ-Fe_2N is assumed to be formed by additional nitrogen atoms going

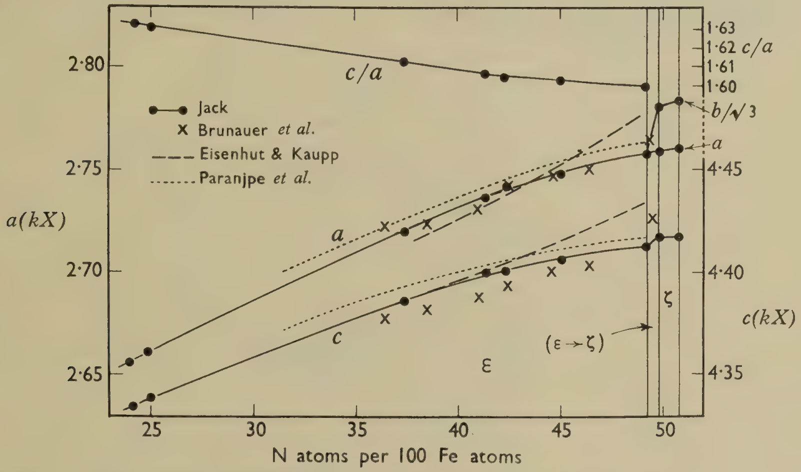


FIG. 51.—Unit-cell dimensions for ϵ and ξ iron nitride phases

into alternate layers giving an AB′AB′... structure as shown in Fig. 53. The true unit cell is hexagonal with the dimension, $a'' = \sqrt{3}.a$ and $c'' = c$, where a and c are the dimensions of the approximately close-packed hexagonal unit of the iron-atom arrangement.

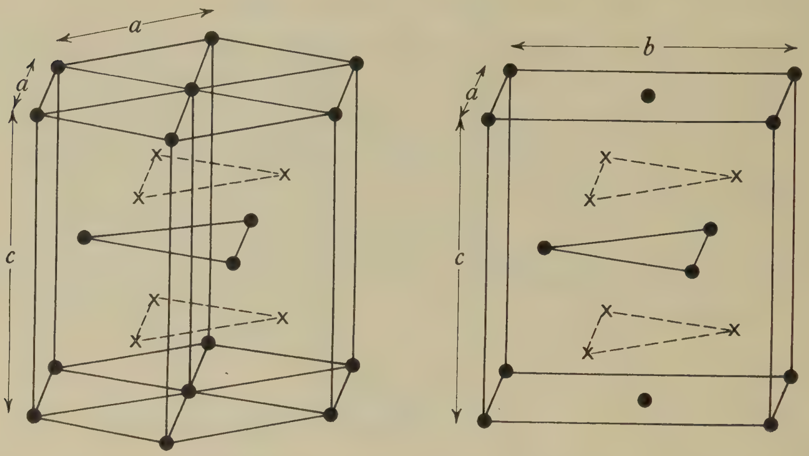
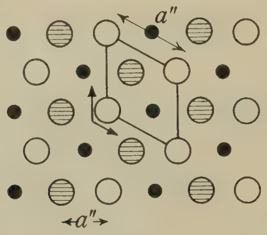


FIG. 52.—Octahedral interstices in ϵ- and ζ- phases

● Metal atom
× Octahedral interstice

When the interstitial-atom concentration of the ϵ-phase is increased from 49·3 to 49·8 nitrogen atoms per 100 iron atoms, there appears to be a marked structural discontinuity.[2] The iron atoms retain the same relative position but there is a small anisotropic distortion of the ϵ-lattice, reducing its symmetry to a new orthorhombic structure, the ζ-phase. The unit cell dimensions of this phase are given by Jack[1] as:



● Occupied in even layer planes *A*
⊜ Occupied in odd layer planes *B*
○ Unoccupied for ε-Fe_3N occupied in *B* layer planes for ε-Fe_2N

FIG. 53.—Layer plane of octahedral interstices in ϵ-iron nitride. Nitrogen atom arrangements proposed by Hendricks and Kosting for Fe_3N and Fe_2N

a = 2·758 kX., b = 4·818 kX., c = 4·416 kX. for 11·1% of N_2

and

a = 2·756 kX., b = 4·820 kX., c = 4·416 kX. for 11·3% of N_2

Refs, p. 233

These values are in good agreement with Paranjpe's dimensions.[4] The structure is such that in each layer plane of octahedral interstices (see Fig. 53) one-half of their number is occupied in a manner that allows each nitrogen atom to have unoccupied holes above and below it in adjacent planes. Each nitrogen atom is surrounded by six iron atoms, two at distances of 1·949 kX. and four at 1·940 kX., giving an average iron–nitrogen distance of 1·943 kX.[1]

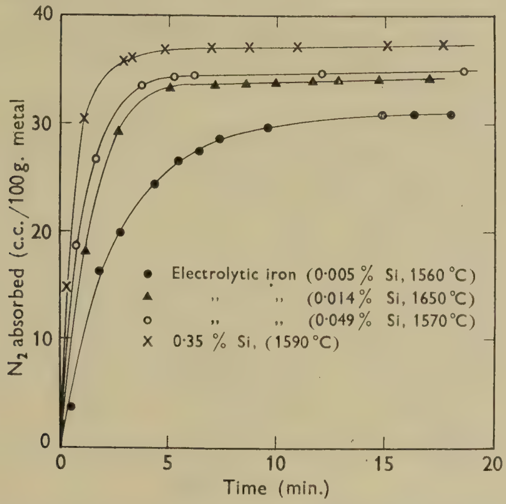


FIG. 54.—Solubility of nitrogen in liquid iron

X-Ray analysis of promoted and non-promoted iron nitride catalysts shows that although the surface area of the former is five times that of the latter, the crystal dimensions are practically the same. The promoter prevents concentration of the crystal nuclei and leads to a more open structure and a larger exposed area.[73]

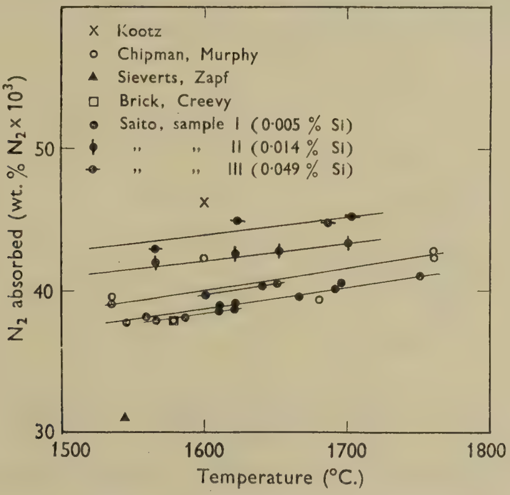


FIG. 55.—Variation with temperature of solubility of nitrogen in liquid iron

SOLUBILITY OF NITROGEN IN LIQUID IRON

The solubility of nitrogen in liquid iron has been reported by several workers.[32, 46–51] The most recent results obtained by Saito[46] for iron with small amounts of silicon impurity are given in Fig. 54, the silicon apparently having an appreciable effect.

The saturation value of iron is given as 0·039 wt.-% of nitrogen at 1600°C. Saito has compared his results with some of the earlier data (see Fig. 55); the results obtained by Chipman and Murphy[47] and by Brick and Creevy[51] are nearly the same, but the two points determined by Kootz[48] and by Sieverts and Zapf[32] differ considerably from the above.

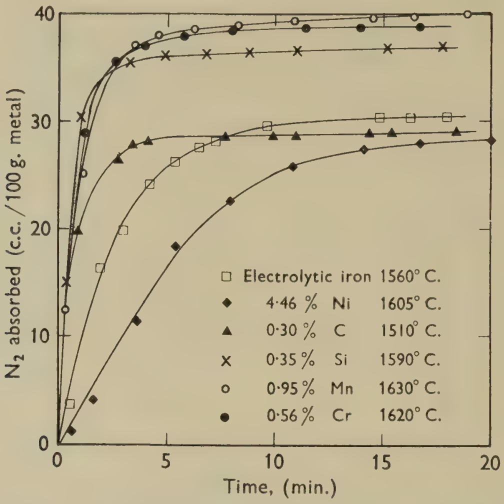


FIG. 56.—Solubility of nitrogen in molten iron alloys

Karnaukhov and Morozov[50] found that the equilibrium solubility of nitrogen in molten iron is strictly proportional to $\sqrt{p}$, when p is the pressure, and deduce that nitrogen either dissolves in iron as dissociated atoms or forms nitrides Fe$_x$N. The rate of solution is proportional to $\alpha-(C_s-C)$, where C_s = concentration at saturation, C = concentration at any given time, and α depends on the rate of removal of nitrogen of Fe$_x$N from the surface into the bulk of the metal.

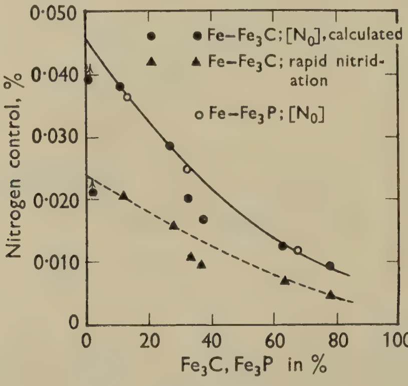


FIG. 57.—Solubility of nitrogen in liquid Fe–C and Fe–P alloys

Figure 56 shows the effect on nitrogen absorption caused by the presence of 0·3% of carbon in the molten iron.[46] Saito has also found that the saturation value of nitrogen decreased with increase in carbon concentration.[52]

The solubility of nitrogen in liquid iron–carbon and iron–phosphide alloys as determined by Kootz[48] is shown in Fig. 57.

Saito's data[46] for the absorption of nitrogen by molten iron containing very small amounts of silicon has been mentioned above: for liquid containing 0·35% of silicon the results are shown in Fig. 56. Saito also observed[51] that in iron–silicon alloys the nitrogen saturation value is a maximum for 0·5 wt.-% of silicon and that a minimum saturation value occurs at a composition corresponding to Fe_3Si: the saturation value then increases again to a composition corresponding to FeSi. Vaughan and Chipman[53] find that an iron nitride and an iron silicide are formed in solution, and that a silicon nitride of limited solubility is formed in the melt. Similar results are reported by Karnaukhov and Morozov,[50] but their data differ; they consider that the nitrogen is dissociated on absorption and forms the nitrides Fe_xN and Si_yN by the following equilibrium processes:

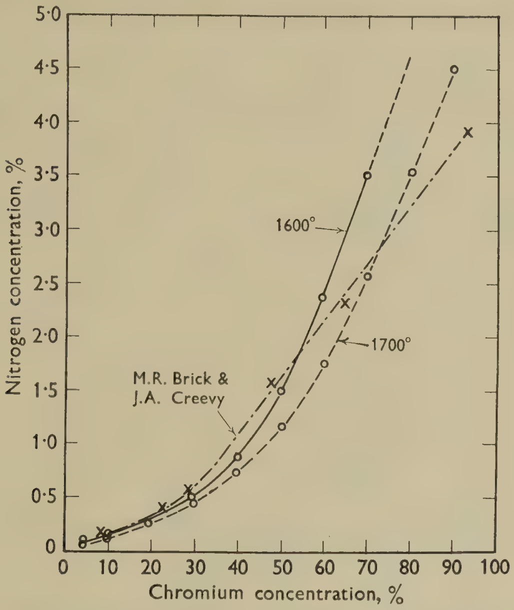


FIG. 58.—Solubility of nitrogen in liquid iron–chromium mixtures

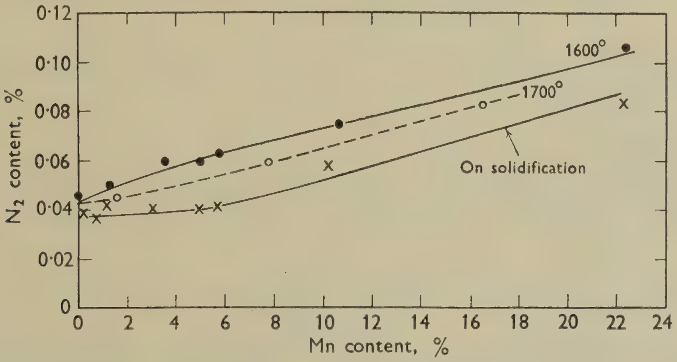


FIG. 59.—Solubility of nitrogen in liquid iron–manganese mixtures

$$Fe_xN \rightleftharpoons xFe + N \quad \text{and} \quad Si_yN \rightleftharpoons ySi + N$$

The only silicon nitride stable in the solution is SiN; hence when Si_2N_3 is dissolved in liquid iron it is decomposed into SiN and nitrogen.

Saito's[46] results for the solubility of nitrogen in liquid iron containing small quantities of chromium, manganese, nickel and carbon are shown in Fig. 56.

Wentrup and Reif[54] investigated the solubility of nitrogen in liquid iron–chromium mixtures (Fig. 58) and also in Fe–Mn (Fig. 59), Fe–Ni (Fig. 60), Fe–Cr–Mn (Fig. 61).

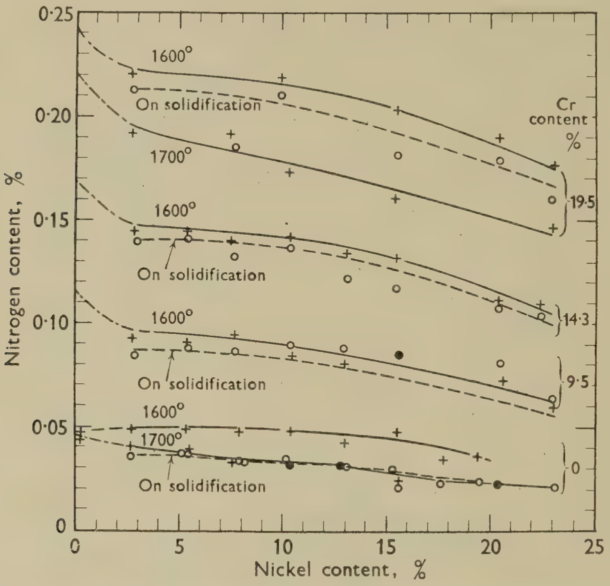


FIG. 60.—Solubility of nitrogen in liquid iron–nickel and iron–nickel–chromium mixtures

and Fe–Cr–Ni (Fig. 62) melts at 1600°C. to 1700°C. and at the solidification points. Fig. 58 also shows the results of Brick and Creevy.[51] Chromium and manganese increase the solubility of nitrogen in iron, while nickel decreases it. Increasing the temperature decreases the nitrogen solubility and at the solidification point nitrogen is evolved. Addition of manganese to iron–chromium melts increases the nitrogen

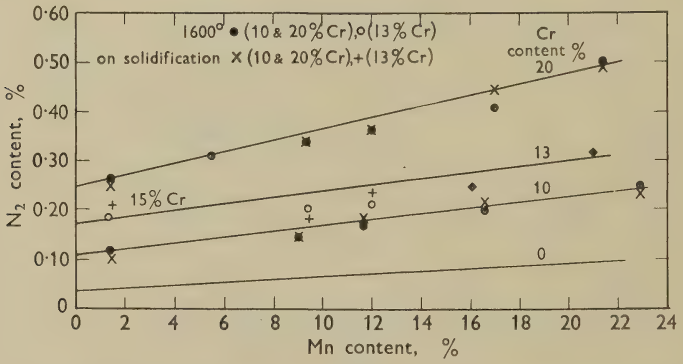


FIG. 61.—Solubility of nitrogen in liquid iron–chromium–manganese mixtures

absorption considerably, whilst adding nickel and raising the temperature reduces the nitrogen solubility. Solidification of Fe–Cr–Mn and Fe–Cr–Ni melts is accompanied by nitrogen evolution.

Data for the solubility of nitrogen in liquid iron–chromium alloys at temperatures of 1550°C. and 1650°C. are reported also by Kurochkin *et al.*[55] Some selected data are as follow:

At 1550°C. and a nitrogen pressure of 735 mm. Hg.

% Cr	3·56	12·60	21·40	40·0	66·0
c.c. N_2/100 g.	58·9	92·2	169·7	453·4	1082·0

At 1670°C. and a nitrogen pressure of 735 mm. Hg.

%Cr	3·36	10·70	21·6	34·0	41·1
c.c. N_2/100 g.	56·9	27·6	151·0	280·0	367·4

At 1550°C and a nitrogen pressure of 572 mm Hg.

%Cr	3·40	10·71	20·4	26·4	44·0	50·5
c.c. N_2/100 g.	44·7	65·6	122·0	168·0	400·5	502·7

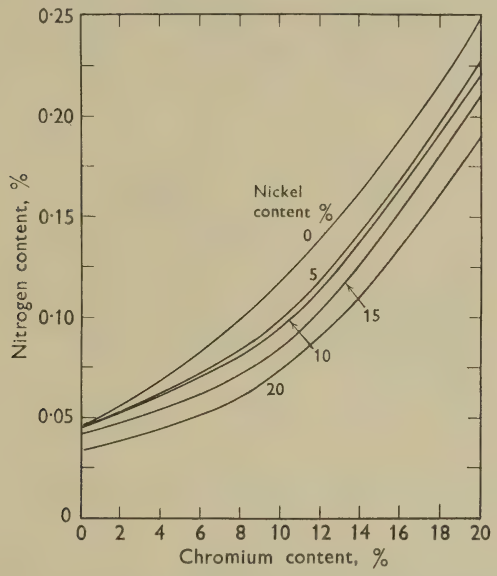


FIG. 62.—Solubility of nitrogen in liquid iron–chromium and iron–chromium–nickel mixtures

For alloys containing more than 10% of chromium these data conform to the equation

$$\log (\mathrm{N}) = K + a \log (\mathrm{Cr})$$

Brick and Creevy[51] found that the relation of solubility of nitrogen in liquid iron–chromium alloys to pressure follows Sieverts' square root law, increase in temperature lowering the solubility. They therefore deduced a reaction of the type

$$x\mathrm{Cr} + \mathrm{N} \rightleftharpoons \mathrm{Cr}_x\mathrm{N}$$

The same authors have investigated also the solubility of nitrogen in liquid iron–vanadium alloys.

Langenburg[56] has reviewed work on the solubility of nitrogen in molten steel and has established a method for its prediction.

Iron Carbonitrides

By chemical and *X*-ray analysis Jack[1, 61] has demonstrated the existence of iron carbonitrides (a series of ternary interstitial alloys) in the reaction products of carbon monoxide with iron nitrides and of ammonia with iron carbides.

Hall *et al.*[62] have also studied the preparation and reactions of iron carbonitrides in the temperature range 250–450°C. Two reactions occur when nitrides are treated with carbon monoxide or carbides with ammonia: a rapid reaction in which carbon or nitrogen enters the lattice until the ratio of carbon and nitrogen to iron atoms increases to about 0·5, followed by a slower substitution reaction in which carbon replaces nitrogen or vice versa. When iron nitrides are treated with hydrogen–carbon monoxide mixtures, the rate of elimination of nitrogen from the components increases with the hydrogen content of the gas, whereas the rate of incorporation of carbon exhibits a maximum when the hydrogen–carbon monoxide ratio is about 1:1. Nitrides are rapidly reduced by pure hydrogen; carbonitrides are reduced more slowly, the rate varying inversely with the carbon content. Nitrogen is removed more rapidly than carbon and the interstitial carbon appears as carbide.

From his results Jack has constructed a ternary diagram (Fig. 63) indicating probable phase fields of the iron–carbon–nitrogen system at 450°C. The ζ-phase carbonitrides have distorted 'normal' 12.*b*.6 structures essentially the same as those of ζ-iron nitrides, with a range of homogeneity extending approximately from Fe_8N_4 to Fe_8C_3N, the distortion increasing with carbon concentration; the latter compound is isomorphous with Fe_2N. ϵ-Phase carbonitrides, prepared as above or by annealing ζ-carbonitrides, have 12.*b*.6 structures and are isomorphous with ϵ-iron nitrides. These compounds have a composition range of approximately 25 to 33 atom-% of nitrogen plus carbon, i.e. from Fe_3X to Fe_2X, in which the higher carbon concentration limit is not less than 16 atom-%.

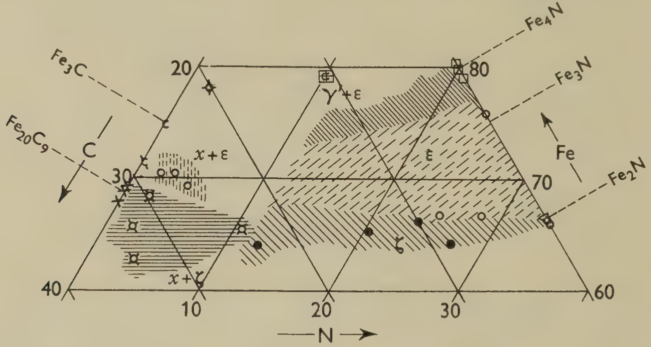


FIG. 63.—Part of the ternary diagram of the iron–carbon–nitrogen system at 450°C. $+ = \alpha$, □ $= \gamma'$, ○ $= \epsilon$, ● $= \zeta$, $\times = \chi$, $C = Fe_3C$

ζ-Carbonitrides decompose in vacuo above 350°C., losing nitrogen and giving ϵ-carbonitride; these are unstable at 450°C. and yield γ' or ϵ-nitrides and iron percarbide or cementite. Jack[61] suggests that reactions in the tempering of martensite are:

$$\text{martensite } \{Fe + C \text{ (interstitial)} + N_2 \text{ (interstitial)}\} \xrightarrow{200°C.} \epsilon\text{-carbonitride}$$

$$\epsilon\text{-carbonitride} \xrightarrow{< 300°C.} \text{Fe percarbide} + N_2 \text{ (dissolved in } \alpha\text{-iron)}$$

$$\epsilon\text{-carbonitride} \xrightarrow{400°C.} \text{cementite} + N_2 \text{ (dissolved in } \alpha\text{-iron)}$$

In carburizing mild steel at 750°C. with carbon monoxide the penetration of carbon is facilitated by previous surface nitriding, and in case-hardening steel by the dry-cyaniding process carbonitrides are probably formed.[61]

Nitrogen in Alloy Steels

Earlier *X*-ray studies of an iron–chromium–nitrogen system are reported by Eriksson.[70] Kurochkin *et al.*[55] found that iron–chromium alloys heated to 1550°C.

with nitrogen at 735 mm. Hg and subsequently cooled in nitrogen contained the following amounts of nitrogen (in c.c./100 g. of alloy):

N_2	144·1	268·0	597·0	1716·0
%Cr	11·8	26·12	41·13	66·15

When the initial conditions were 1550°C. and 512 mm. Hg the solubilities were:

N_2	101·8	140·0	230·0
%Cr	13·34	19·75	27·0

Krainer and Mirt[64] observed that the addition of nitrogen to steels containing more than 18% of chromium produced in casting alloys a better structure, less grain-coarsening on welding and greater toughness after annealing at high temperatures. The chromium-nitrogen steels can be produced by saturating carbon-poor ferrochromium with ammonia at 700–900°C.; the resulting nitrogen content of the steel amounts to some 1/75 of the chromium content. These studies are presented in Fig. 64 as a section through the iron corner of the Fe–Cr–N diagram (Cr:N ≡ 75:1). An earlier phase diagram for this system is reported by Yazykov *et al.*[63]

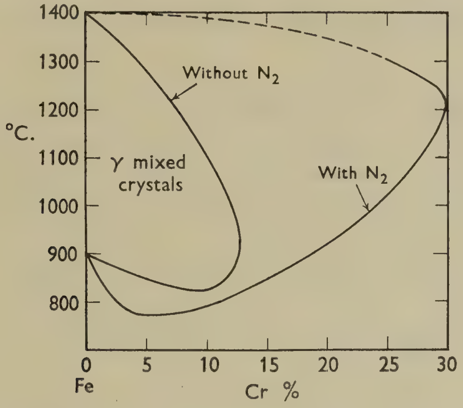


FIG. 64.—Solubility of nitrogen in iron–chromium alloys

The phase limits for steels containing 10–35% Cr, 2–23% Mn and 0·11–0·44% N have also been investigated.[64] For the system Fe–Cr–Ni–N_2 phase distributions 1200°, 800°, 650° and 20°C. show that new phases do not occur in Cr–Ni–N steels as in the case of pure Cr–Ni steels, although the ranges of the individual phases differ.[65]

Further data on the effect of nitrogen on iron alloys containing aluminium[63] and molybdenum[66, 67] are reported. Sieverts and Bruening[67] showed that for the pressure range 100–760 mm. Hg and at temperatures from 300–1100°C., the nitrogen absorbed at constant temperature is proportional to the square root of the gas pressure. Below certain limiting temperatures very large quantities of nitrogen are absorbed by alloys containing 6·1–8·7 atom-% of molybdenum.

The system iron–nickel–nitrogen has been investigated.[71] Alloys of iron and nickel containing 10 to 95 atom-% were nitrided between 300° and 1000°C. in a stream of ammonia. The optimum temperature range for uptake of nitrogen was 350–600°C. The weight-% of nitrogen in the nitrided alloys varied linearly with the iron content. The uptake of nitrogen can be increased further by pretreatment of the alloy with ammonia at 600–800°C., quenching to room temperature and finally further nitriding at 400–500°C. For alloys treated in this way which contain 50% or more of iron the percentage of nitrogen again varies linearly with the percentage of iron; with alloys containing less iron the percentage of nitrogen approximates to that for Fe_4N. *X*-Ray analysis of the pure and nitrided alloys shows that two alloy and two nitride phases are formed. A face-centred cubic phase occurs in alloys containing

10–70% Fe, and is the only phase if the nitrogen is below 5%. This phase resembles γ-iron in dissolving nitrogen with an increase in the lattice constant a. A body-centred cubic phase is stable for an iron content above 70%, with nitrogen up to 3% and nitriding temperatures up to 450°C.; above 450° it changes to the face-centred cubic phase mentioned above, but with a greatly enlarged lattice, like α-iron; the body-centred cubic alloy takes up very little nitrogen in solid solution. A cubic face-centred nitride phase is stable up to 70% of iron, while above this a hexagonal nitride phase also occurs. The face-centred cubic nitride phase corresponds to Fe_4N with some of the iron replaced by nickel; the constant a increases with the percentage of nitrogen and its increase with the percentage of iron parallels that for the pure alloys. The hexagonal nitride phase resembles Fe_2N except that a little of the iron is replaced by nickel. The decomposition temperatures of the nitrided alloys increase from 360 to 500°C. with increase in the percentage of iron.

The reader is referred also to the work of Pearson and Ende[113] who have evolved a semi-theoretical method for calculating the dissolved nitrogen content of alloy steels. Other reviews up to 1943 of some of the data on ternary alloys of iron and nitrogen have been reported.[7, 8]

The mechanism of the thermal dissociation of activated and non-activated iron nitrides and the relationship to ammonia synthesis and the Fischer–Tropsch reaction have received some attention.[72, 80–91]

Kinetics of Decomposition of Iron Nitride

Goodeve and Jack[72] have studied the kinetics of nitrogen evolution from ϵ-iron nitride. On heating at temperatures below 500°C. ϵ- or ζ- iron nitrides in carbon monoxide almost three-quarters of the original nitrogen atoms are gradually and isomorphously replaced by carbon atoms with only minor dimensional changes in crystal structure. The nitrogen is evolved mainly as nitrogen molecules and partly as cyanogen. On heating the nitrides in a hydrogen atmosphere at temperatures of 250–450°C. the nitrogen is eliminated entirely as ammonia. These authors observed that the rate-determining process for the decomposition of ϵ-iron nitride at 350–500°C. is the same in vacuo, in molecular nitrogen and in carbon monoxide. The rate obeys a kinetic equation of the second order with respect to the interstitial nitrogen concentration and is associated with an activation energy of 42,100 ± 1400 g.-cal./g-mol. The velocity of diffusion of the nitrogen atoms to the surface is at least 10^4 times as rapid as the rate determining process, which is believed to be the combination of pairs of nitrogen atoms at the solid surface.

THERMODYNAMIC CONSTANTS OF IRON NITRIDE

In an investigation of the specific heats of the nitrides of iron over the temperature range 0–99·7°C. Satô[93–97] found a maximum at 9·7% nitrogen. For Fe_4N he calculated a specific heat $C_p = 29{\cdot}48$ at 320°C. Using this value Kelley[112] deduced the equation:

$$C_p = 26{\cdot}84 + 8{\cdot}16 \times 10^{-3}T$$

for the variation of C_p with temperature and reported the heat and free energy of formation of Fe_4N as:

$$\Delta H_{298\cdot 1} = -2550 \text{ g.-cal./mole}, \qquad \Delta G_{298\cdot 1} = 890 \text{ g.-cal./mole}$$

Pearson and Ende[113] report that the variation of ΔG with temperature follows the equation:

$$\Delta G_{(298-860°K)} = -5800 + 24{\cdot}5T$$

On the basis of Satô's interpolated specific heat of Fe_2N as $C_p = 16{\cdot}88$ at an average temperature of 323°, Kelley[112] calculated that the variation of specific heat with temperature for the nitride is given by:

$$C_p = 14{\cdot}91 + 6{\cdot}09 \times 10^{-3}T$$

The heat and free energy of formation of this nitride are calculated to be $\Delta H_{298 \cdot 1} = -920$ and $\Delta G_{298 \cdot 1} = 2580$, but Kelley considers that little significance can be attached to these figures and therefore recommends no values for Fe_2N.

An *X*-ray determination of the linear coefficient of expansion of Fe_4N gives a value of $0{\cdot}79 \times 10^{-5}$ between 18° and 386°C., and that of Fe_2N as $2{\cdot}22 \times 10^{-5}$ between 18° and 420°C. compared with $1{\cdot}33 \times 10^{-5}$ for iron.[98] Some studies of the specific gravity of Fe_2N and Fe_4N are reported.[99–101]

Sieverts and Krüll[101] give:

Fe_2N	$\%N_2$	1·1	9·1	7·0	6·7
	d_{25}	6·501	6·742	6·746	7·073
Fe_4N	$\%N_2$	5·7	3·0		
	d_{25}	7·110	7·507		

The specific magnetization (σ) follows the law

$$\sigma_h = \sigma_\infty \left\{1 - \frac{a}{H}\right\}$$

where $a = 356$ and 420 at 290°K., and 77°K. respectively. (For the iron used in the preparation $a = 300$ at 290°K.) If all the iron atoms in Fe_4N are identical, the magnetic moment of the iron atom is 10·00 Weiss magnetons. The Curie point is 488°.[102]

On bombarding an ϵ-phase nitride (composition between Fe_3N and Fe_2N) with electrons, it was observed that the yield of gas per electron increased from 0·005 molecules at 4 v. to 1·2 mols. at 120 v.; sharp increases took place at 7, 10 and 17 v. These potentials are supposed to be the critical potentials of iron nitride.[103]

Nitrogen diffuses more easily in α-iron than in γ-iron.[104, 105] The diffusivity of nitrogen in α- and γ-iron at various temperatures is given in Table VII.[105]

Table VII.—Diffusivity of Nitrogen in Iron

Temperature, °C.	*D*, Experimental cm.^{2} per sec.
9·5	$2{\cdot}4 \times 10^{-17}$
21·5	$1{\cdot}1 \times 10^{-16}$
500	$3{\cdot}8 \times 10^{-8}$
600	$1{\cdot}4 \times 10^{-7}$
950 (α-iron)	$3{\cdot}1 \times 10^{-6}$ (calculated)
950 (γ-iron)	$6{\cdot}5 \times 10^{-8}$

The diffusivity of nitrogen ($D_n(\alpha)$) in α-iron conforms to the equation

$$D_n(\alpha) = D_0\, e^{-E/RT}$$

where $E = 18{\cdot}6$ kcal./mole and $D_0 = 6{\cdot}6 \times 10^{-3}$.[105] Other workers report that the temperature-independent factor D_0 is 3×10^{-3},[106] or $1{\cdot}4 \times 10^{-3}$ cm.^{2}/sec.,[107] and that the value of *E* is 17·7 kg.-cal./mole[107] and 17·2 kcal./mole.[108] Further work on the diffusion of nitrogen in iron, steel and synthetic ammonia catalysts has been reported.[109, 111]

Much other work relating mainly to the more metallurgical aspects of nitrogen in iron and various types of steel has been described.[114–202] Reviews dealing with specific aspects of the nitrogen–iron and nitrogen–steel systems have also been presented.[203–205]

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Nitrides of Cobalt and Nickel

COBALT NITRIDES

Nitrogen is almost insoluble in cobalt at temperatures up to 1200°C.[1] At 600°C. the solubility of nitrogen in α-cobalt is 0·6%.[2]

The nitride Co_2N is obtained by the reaction of ammonia with cobalt produced by the reduction of Co_3O_4 in hydrogen.[2] It was found difficult to remove all the oxygen content and about 0·2% was left after reduction at 900°C. The best nitridation temperature for preparing Co_2N was 380°C. Pure Co_3N could not be prepared by nitridation but was obtained by thermal decomposition of Co_2N at 276°C.[2, 3]

The nitride Co_3N has an interstitial structure with a hexagonal and metallic lattice, $a = 2{\cdot}658$ A., $c = 4{\cdot}351$ A.; it has only a narrow range of homogeneity, being stable between 7·7 and 8·0 wt.-% of nitrogen.[2]

The nitride Co_2N has a rhombic deformed hexagonal close-packed structure, with $a = 2{\cdot}842$, $b = 4{\cdot}627$, $c = 4{\cdot}330$ A.[2] It is isostructural with Co_2C and the lattice parameters are $a = 2{\cdot}8535$, $b = 4{\cdot}6056$, $c = 4{\cdot}3443$ A.; the arrangement is different from that in Fe_2N.[3]

According to Schmitz-Dumont *et al.*[4] cobalt amide, $Co(NH_2)_3$, when heated isothermally at 40–50°C., decomposes irreversibly to give ammonia and black pyrophoric amorphous CoN. Attempts to prepare crystalline CoN by heating $Co(NH_2)_3$ in an autoclave filled with liquid ammonia for 4–10 days at higher temperatures were unsuccessful. Under these conditions amorphous products were obtained for which the Co:N ratio decreased from 1:1 at 94° to 1:0·5 at 150° and to 1:0·28 at 200°C. In neutral or alkaline solution CoN decomposes to give ammonia and a cobaltous compound, while in dilute sulphuric acid the nitrogen appeared both as such and as ammonium sulphate; gaseous nitrogen was the only product from the nitride having the lowest Co:N ratio. Hydrogen was also a product of the reaction of the lower nitrides with dilute sulphuric acid, although it was not observed in the CoN reaction.

Carbon monoxide at 340°C. gradually reacts with Co_2N and with Co_3N to form the corresponding carbonitrides. *X*-Ray analysis of Co_2N, $Co_2C_{0{\cdot}53}N_{0{\cdot}47}$, and Co_2C shows that the unit cell dimensions of cobalt carbonitrides change gradually as carbon is replaced by nitrogen.[3] Heating Co_3O_4 in ammonia at 330–390°C. for 2–3 hours leads to a replacement of oxygen in the CoO lattice by nitrogen, with a resulting nitrogen content varying from 3·9 to 7·9%.[2]

In order to explain certain anomalous properties of cobaltous amide it is suggested that it could be regarded as an ammonia–cobaltous nitride complex, i.e. $Co_3N_2 + xNH_3$.[5]

NICKEL NITRIDES

Nitrogen does not react with nickel at temperatures up to 900°C.[6] Nickel sputtered under special conditions gives a nitride film which decomposes on heating to 350°C.[7]; when heated to 150°C. in hydrogen, ammonia and nickel are formed. From an *X*-ray study it has been established that the solid solubility of nitrogen in nickel does not exceed 0·07%.[8]

Thermal decomposition of $Ni(NH_2)_2,2NH_3$ (prepared by the action of potassium amide, KNH_2, in liquid ammonia at 33·5°C. on cationic nickel salts) at 10^{-3} mm. Hg produces successively $Ni(NH_2)_2$ at 42·3°C., Ni_3N_2 at 119·3°C., Ni_3N at 362°C. and Ni and N_2 at 585°C.[9] By passing a rapid stream of ammonia over nickel powder Ni_3N is prepared[8]; it can also be prepared from $NiF_2,2NH_4F$ or from nickel bromide, but there is no particular advantage in using the halides.

By heating nickel on thoria at 170°C. in ammonia a compound with the limiting formula Ni_3N is obtained; this substance is paramagnetic and has a hexagonal lattice.

The nitride Ni_3N is a dark grey substance, easily ground in an agate mortar, and stable to oxygen and moisture. Neither hot nor cold sodium hydroxide solution affects it. Acids and acid solutions react, slowly to explosively according to the concentration and temperature. Its density at 25°C. is 7·66 g./c.c., which is lower than the value 7·91 g./c.c. calculated from *X*-ray data. The nickel atoms form a hexagonal close-packed lattice, $a = 2{\cdot}66$, $c = 4{\cdot}298$ A., $c/a = 1{\cdot}613$, the nitrogen atoms being present in the nitride interstitially. The structure is isomorphous with the ϵ phase of Fe_3N and ϵ-Fe_3CN[9, 11] and is quite different from that of Cu_3N. The nitrogen atoms are located at the centre of an octahedron of nickel atoms at a distance of 1·877 A. from the nickel atoms and 3·423 A. from the other nitrogen atoms. The unit cell dimensions are $a = 2{\cdot}667 \pm 0{\cdot}0005$ A., $c = 4{\cdot}3122 \pm 0{\cdot}0005$ A., $c/a = 1{\cdot}6165$.[11] The nitrogen of nickel nitride may be partly replaced by carbon to form a nickel carbonitride with only small dimensional change. Nickel nitride decomposes at 155°C. in hydrogen or at 450°C. in nitrogen.[10]

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SECTION IV

THE OCCURRENCE, PREPARATION AND PRODUCTION OF AMMONIA

(other than by the Haber Process)

BY G. S. CRIBB

As is evident from the original treatise (Mellor, VIII, 146), the occurrence in nature of ammonia and nitrogenous substances capable of yielding ammonia is widespread. The gas may be prepared or produced in small quantities from many sources.

OCCURRENCE AND SMALL SCALE PREPARATION OF AMMONIA

Ammonia was originally thought to be present in the atmosphere during the early stages of the evolution of the earth, but later calculations, based on equilibrium constants for reactions between gases and their solubility in water, indicate that an atmosphere of carbon dioxide and nitrogen was predominant.[2] The presence of ammonia in the solar spectrum could not be established by two investigators,[3] who doubted whether lines identified by other workers arose from atmospheric absorption. On the other hand, the atmospheres of Jupiter and Saturn are known to contain ammonia and methane.[4, 5] Aerosols present in the atmospheres of Central Europe and the Atlantic coast of America consist almost entirely of ammonium and sulphate ions, when the particle size ranges from radius 0·08 to 0·8 microns.[6] The fact that the concentration of nitrogen compounds, including ammonia, is greater in the summer, and in the tropics as compared with cooler zones, leads to the conclusion that nitrification is influenced by photochemical reactions.[7] Another observer reports nitrogen precipitation as being higher in the summer, and states that on the average 56% of the nitrogen is present as ammonia.[8] The irregular distribution of ammonia in sea water is tentatively explained by its adsorption on randomly distributed particulate matter.[9]

The only reported sources of naturally occurring ammonia from which the gas is recovered commercially are the borax bearing geysers of Tuscany. The ammonia content of this natural steam is given as 0·019%,[10, 11] the availability of the steam being about 3 million pounds per hour in 1939[12] with power capacity equal to 254,520 kW. in 1951.[11] Ammonia in concentrations of 1–60 mg./l. is found in the hot springs of the Aso Volcano in Japan,[13, 145] the content varying with the rainfall.

From Elemental Nitrogen

The main industrial production of ammonia, described elsewhere (see page 259), is by the fixation of nitrogen in the Haber Process. Nitrogen may also be fixed by forming cyanides or calcium cyanamide, which are hydrolysed to yield ammonia (Mellor, VIII, 164). An article in 1926 describing the production of cyanide from coal, alkali and nitrogen and its subsequent hydrolysis suggests the process as worthy of consideration for the production of ammonia.[15] There are many references to this process in the literature up to 1933, but very few since that date, indicating that it is now only of historic interest.

Many variations of the cyanide and cyanamide processes are given in patents, such as the use of barium oxide and hydrogen in a cyclic process,[16] the production of oxalate and formates as by-products,[17] the use of iron carbonyl and hydrogen,[18] reduction with coke-oven gas giving hydrogen cyanide as a by-product,[19] incorporation of an alkali fluoride in cyclic processes[20, 21] and the preparation of pure liquid ammonia from crude calcium cyanamide.[22] The cyanogen compounds in fuel gases, such as hydrogen cyanide, are converted into ammonia by passing them over heated catalysts.[23–25] The addition of calcium fluoride to pure molten calcium carbide has been found to increase the rate of nitrogen fixation.[26] Variations have been proposed to the Le Blanc[27–29] and ammonia–soda[30] processes for the production of sodium carbonate, which yield ammonia as a by-product. A review in 1928 describes some of the problems associated with the conversion of cyanide to ammonia, which hampered the development of the process to the scale required.[31]

Ammonia is also obtained from elemental nitrogen in the preparation of phosphorus,[32, 33] in the removal of nitrogen from combustible gases by lithium–mercury amalgam[34] and in the initial stages of the operation of columns packed with active copper for the removal of oxygen from oxygen–nitrogen mixtures.[35] Three instances of the recovery of ammonia from inorganic nitrogen compounds are the electrolytic reduction of sodium nitrate,[36] the treatment with sodium hydroxide in an autoclave of aluminium dross which contains aluminium nitride[37] and the reduction of alkali metal nitrates by solid non-metals in the presence of dry alkaline earth hydroxides.[38]

From Ammonium Salts

The ammonium salt generally employed for the production of ammonia is the chloride. Two cyclic processes for the separation of ammonia and hydrogen chloride from ammonium chloride are described, one using magnesium oxide[39] and the other molten sodium bisulphate.[40] An earlier German patent recommends treating the chloride with alkaline earth oxides or hydroxides in the presence of liquid ammonia.[41] Experiments carried out with perfectly dry quicklime and ammonium chloride[42] indicate that the presence of moisture is essential for the liberation of ammonia at ordinary temperatures. In the absence of moisture a temperature of 120–130° is necessary to start the reaction. Ammonia and pure chlorine can be obtained by the electrolytic decomposition of aqueous ammonium chloride solutions, if appreciable quantities of an alkali chloride or alkaline earth chloride are present.[43, 44] Two patents[45, 46] describe the production of a mixture of ammonia and acetylene, for use as a motor fuel, by heating a mixture of ammonium chloride, lime and calcium carbide.

Ammonium thiocyanate decomposes on heating with steam, or with water under pressure, at temperatures above 200°.[47] Pure anhydrous ammonia can be obtained by distilling ammonium hydroxide, absorbing the gas in ammonium cyanide and then liberating it by reheating.[48] For use as a microreagent a pure solution can be obtained by an isothermal diffusion method.[49] On the larger scale pure concentrated aqueous ammonia is formed by grinding ammonium sulphate crystals with lime and a little water in a gas-tight closure, passing steam continuously into the reacting mass, rectifying the issuing vapours and condensing the fraction enriched with ammonia.[50]

From Organic Matter

Ammonia may also be obtained from nitrogenous organic matter. It is liberated in the evaporators during the concentration of raw sugar juices extracted from beet.[51–53] The bacterial decomposition of the nitrogenous matter accompanying the respiration of (i.e. conversion of oxygen to carbon dioxide by living organisms present in) 200 g. of raw sugar yielded 1–7 mg. of ammonia in ten days at 20°C.[54]

Methods have been described[55, 56] for recovering ammonia from this source, and also from the products resulting from the dry distillation of vinasses.[57–59]

In Switzerland ammonia and urea are recovered commercially from pine-wood during the fermentation of the glucose solution obtained by saccharification of the wood with acid as a catalyst.[60] Methods are described in the original treatise (Mellor, VIII, 165) for the preparation of ammonia from various nitrogenous wastes, and developments have taken place in the following methods: the destructive distillation of leather scrap,[61] and the incineration and dry distillation of sewage sludge, animal and agricultural wastes.[62–67] Ammonia is evolved also in the dry distillation of exhausted 'foots' from olive-oil production,[68] in the retting of hemp[69] and in the pyrolysis of molasses to give liquid fuel.[70] Many proteins yield ammonia when they are subjected to hydrolysis or oxidation. It is probable that hydrolysis is the final step in the formation of ammonia by the action of oxidizing agents on nitrogenous substances.[71] This breakdown of protein by oxidation is stated to be the process by which leather is aged, the rate of oxidation being increased by iron salts.[72]

RECOVERY OF AMMONIA IN THE PROCESSING OF FUELS

Ammonia is liberated when nitrogenous fuels such as coal, peat and shale oil are subjected to one or more of the processes of distillation, gasification and hydrogenation. The principal source of non-synthetic ammonia is the carbonization or distillation of coal in the absence of air, as in the manufacture of coal gas and of coke in coke ovens (Mellor, VIII, 166). The economics of by-product ammonia recovery in England were profoundly affected by the advent of the synthetic ammonia process, which developed rapidly after 1926.[73] The revenue derived from sulphate of ammonia and ammonia liquor by three large gas companies in the London area declined from an average profit of 11*d.* per ton of coal carbonized in 1926, to a loss of 0·48*d.* in 1932, when the price of the sulphate fell to £5 5*s.* per ton. Although the price subsequently rose, articles published after this period in Germany,[74] Italy[75] and the United States,[76] as well as in the United Kingdom,[77] claim that recovery of by-product ammonia is uneconomic. Ammonia must be removed from the gas, however, since it is an impurity, and the ammoniacal liquors form an undesirable effluent.[78] In many cases, therefore, ammonia recovery is essential even if it constitutes a charge on the gas-making process. The effect of the decreased revenue has been to bring about improvements in the methods of recovery, centralization of ammonium sulphate manufacture and recovery of the ammonia in an alternative form.[79, 80] Evidence of the continued recovery of ammonia is obtained from the Annual Reports of the Alkali Inspector,[81] which give the figures recorded in Table I for sulphate and liquor production, expressed as 25% ammonia, by gas works in England and Wales.

Table I.—Industrial Recovery of Ammonia: tons of 25% *ammonia liquid*

	1930	1932	1938	1942	1947	1956
Recovered from Gas Works	199,751	124,700	167,100	114,300	133,600	206,900
Total Ammonia Production	730,508	726,300	663,400	1,272,000	2,204,900	3,254,900

(Up to and including 1938 tonnages were based on 25·75% ammonia, and the above figures have been corrected to the basis of 25% ammonia. Quantities for the recovery from gas works up to and including 1942 include ammonia liquor from coke-ovens, but this probably does not account for more than about 12% of the total amount.)

Refs. p. 250

The figures in Table I show that while ammonia recovery in the gas industry has returned to the level of 1930, it now (1960) represents less than 7% of total production compared with over 25% in that year. Over this period the quantity of coal carbonized has increased by approximately 50%.[82]

Yields of Ammonia from Coal and Peat

The yield of ammonia from coal is dependent on a number of factors. For example, in a study of fifty-eight American coals,[83] the average yields of ammonia were as stated in Table II, expressed as pounds of ammonium sulphate per ton of coal carbonized.

Table II.—Yields of Ammonia in the Gasification of Coal

Temp., °C.	800°	900°	1000°
1. High volatile coal	22·5–35·9	19·6–30·1	15·5–27·4
2. Medium volatile coal	21·9–27·0	18·0–24·4	12·0–19·2
3. Low volatile coal	17·5–19·2	14·0–14·9	9·0– 9·2

Many other workers[84–93] have reported the effects of the percentage of volatiles in the coal and of the carbonization temperature. Generally the yield of ammonia increases with temperature up to 700–800°C.[86, 92] and then decreases. Other factors influencing the yield of ammonia are prior oxidation of the coal,[94] the presence of hydrogen, steam or nitrogen,[93, 95–98] the carbonization pressure,[88, 98] prior washing of the coal,[99] the size of the retort,[100] the addition of inorganic compounds such as iron oxide, lime and soda ash;[85, 86, 101] the duration of carbonization,[92, 102] the grain size of the coal[85] and the blending of coals.[103, 104] The evolution of ammonia occurs principally in the third or 'finished-coke' zone.[105]

A greater conversion of the nitrogen in coal to ammonia is brought about by the processes of hydrogenation and gasification, as opposed to carbonization. The pressure gasification of South African coal by the Lurgi process yields 18 lb. of ammonia per ton,[106] and a United States patent claims that all the nitrogen may be converted into ammonia.[107] In experiments on the high-temperature hydrogenation of an Indiana coal, ammonia production ranged from 6·7 to 22·4 lb. per ton; the latter figure represents almost complete conversion of the nitrogen into ammonia.[108] A study of coal hydrogenation[109] indicates that the formation of ammonia differs from the other reactions involved. The explanation is thought to lie in the central location of the nitrogen atoms within the coal structure so that rupture of many C–C bonds precedes that of C–H bonds. In a study of the generation of producer gas from anthracite and coke,[110] the yield of ammonia was greatly increased by the addition of sodium carbonate but was not affected by steaming. Samples of producer gas generated from charcoal contained 0–0·024% of ammonia.[111] The organic nitrogen content of the crude light oil obtained in the purification of coke oven gas may be converted into ammonia by pressure hydrogenation of the oil, using the gas itself as the source of hydrogen.[112]

Many attempts have been made (Mellor, VIII, 166) to recover ammonia from peat without success. Recovery on a commercial scale has been reported, principally from Russian sources,[113–117] but also from Western Europe.[118] The yield from the last source is stated as 5 to 8 kg. of ammonia per ton of dry peat, whereas the peat generators in the U.S.S.R. yield 12 to 18 kg. of ammonia per cu. m. of waste water. About 0·15 cu. m. of waste water is derived from 1 ton of peat, but it is not stated whether the basis is dry peat. The effect of the method of carbonization on the yield of ammonia is given in a review of the economics of peat utilization.[119] A method of utilizing ammonia *in situ* during the burning of moorland soils is described[120]: the ammonia liberated from the burning layer of peat and from that immediately beneath it is absorbed by the unburnt peat and acts as a fertilizer.

Refs. p. 250

Recovery of ammonia from the retorting of oil shale was the principal source of ammonia production in Scotland up to 1946. The installations in Scotland,[121] Sweden[122] and Australia[123] have been described.

Recovery of Ammonia from Coal Gas

There are three principal methods by which ammonia is recovered from gases produced by the carbonization of coal; the indirect, the semi-direct and the direct. In the indirect method (Mellor, VIII, 166) the ammonia is collected in the form of a liquor from the hydraulic main, the condensers and the ammonia washers. This liquor is steam-distilled with or without the addition of lime and the vapours passed into a saturator, where the ammonia is absorbed by sulphuric acid and the acid constituents pass on. The disadvantage of this method was the large volume of effluent produced, but by adequate cooling of the gas and fractional condensation of the virgin liquor the addition of water may be partially or completely eliminated.[124] The complexity of this process led to the introduction, in the coke-oven industry, of the direct method whereby the gas, while still above the dew point, was passed directly into sulphuric acid. Sensicle[125] advocated this method for the gas industry, as a solution to the problems arising through competition from synthetic ammonia and increased effluent restrictions. The advantages claimed were lower capital and operating costs and less effluent, but the suggestion was rejected by others. Parrish[126] drew attention to the corrosion caused by the decomposition of ammonium chloride in the saturators, the unsatisfactory nature of the tar recovered and the inferior quality of the sulphate. Other objections, raised by Parker,[127] were the inability of saturators to deal with fluctuating gas loads, the additional power required to pump hot saturated gas through the saturators, the increased risk of naphthalene deposition by the removal from the hot gas of tar which acts as a solvent and the increased quantity of acid constituents remaining in the gas. The difficulties associated with the presence of ammonium chloride and tar in the saturators led to the development of the semi-direct process. This involves a preliminary cooling of the gas to remove tar, fixed ammonia, some free ammonia and most of the water. The virgin liquor is separated from the tar, distilled, and the ammonia vapours are combined with the gas and passed to the saturator. The semi-direct process is used extensively in the coke-oven industry[128] and is the subject of many patents.[129–137] Parker[127] claimed, as with the direct process, that it offers no financial advantage to the gas industry over the indirect process, but Foxwell[138] challenged this statement. An application of this method to ammonia recovery on a gasworks has been described,[139] but because of its greater flexibility the indirect method has not been superseded in the gas industry. One objection to the direct method was overcome by the introduction of the electrostatic precipitator,[140] which effectively removes tar from the hot gas and so obviates cooling.

Recovery by Indirect Methods

AMMONIA ABSORPTION

The two unit operations involved in the indirect method, viz., the absorption of the ammonia from the gas and its subsequent recovery by distillation, have been studied in great detail. To recover ammonia economically, the volume of water associated with the ammonia removed from the gas must be kept to a minimum.[78, 141] The hot gas leaving the carbonization zone is cooled, from approximately 600° to 80°, by the adiabatic evaporation of water from weak ammoniacal liquor sprayed into the gas offtakes.[142–144] Most of the ammonium chloride and tar are removed at this stage, the unevaporated liquor being recycled after separation from the tar and further weak liquor added to replace that lost by evaporation. It has been suggested that water, not ammonia liquor, should be used for this purpose, but the reasons given are not valid.[145] The hot saturated gas passes to the condensers where an ammoniacal liquor condenses,[146] the residual ammonia in the gas being reduced to 5 grains per 100 cu. ft. by counter-current contact with water or weak liquor in a suitable washer.[147, 148] Variations of this method include washing under pressure,[149] washing with the liquor rich in fixed ammonia,[150–153] and recycling part of the condensate to irrigate the gas passes of the condenser.[154] In the cyclic process operated on Russian coke ovens, the cooling and washing stages are carried out in a single direct-contact scrubber-cooler irrigated with cooled effluent from the distillation stage.[155–157] An extensive theoretical treatment of the design and performance of washers for the recovery of ammonia was given by Hollings and Silver in 1934.[158] The variables involved are the interfacial area of gas–liquid contact, the concentration or partial pressure driving force for diffusion and the mass transfer coefficient which incorporates the diffusivity. Similar treatments have been proposed by other workers.[159–162] In the gas industry multi-stage washers are usually employed for ammonia recovery, because of the low liquor to gas ratio required. Stage efficiencies for such a washer, based on the method of Silver, have been given as 55%.[163] Claims have been made as to the relative merits of certain types of washer, although the basis for comparison is not always clear. Operating costs for mechanical absorbers have been reported as below those for hurdle or grid-packed scrubbers[164, 165]; in a later reference,[166] however, it is stated that on the basis of absorption coefficient mechanical scrubbers and packed scrubbers are equivalent, but both are inferior to bubble cap columns. Additional evidence for the superiority of bubble plate columns is given,[167] but it is claimed elsewhere[168] that spray towers are eight times as effective. A reduction in the absorption coefficient in a scrubber, through failure to ensure adequate liquid distribution over the packing, has been observed.[169] This is reflected in the comparative area requirements of hurdle scrubbers and rotary scrubbers.[170] Washers suitable for ammonia recovery, other than those referred to, have been described in patents[171, 172] and in the technical literature.[173, 174]

Calculations for the design and estimation of the performance of an ammonia washer require a knowledge of the vapour pressure of ammonia above the wash liquor.[175] Equilibrium data have been presented in the form of curves for ammoniacal liquors[176, 177] and vapour pressures have been determined in the laboratory for ammonia and carbon dioxide over solutions of the constituents of such liquors.[178] These vapour pressure data, supplemented by further experimental determinations, have been correlated in terms of the ionic equilibria existing in the solutions.[179] More recently two further sets of data have been published,[180, 181] the first substantiating the results of earlier work.[178] It has been pointed out, however, that in an ammonia washer the wash liquor is far from being in equilibrium with the gas as regards carbon dioxide and hydrogen sulphide.[182, 183] The complexity of the simultaneous absorption of ammonia and carbon dioxide has been stressed by Bramslev[184] and the kinetics of the absorption process have been studied by a number of workers.[185–187] Certain recommendations have been made regarding the operation and control of ammonia washers so as to obtain the maximum strength of liquor combined with adequate purification of the gas.[188–193] An important contribution in this respect is the proposal to carbonate the weak ammoniacal liquor prior to its use in the ammonia washer.[194]

CONCENTRATION OF THE AMMONIA LIQUID

The crude ammoniacal liquor obtained from the condensers and ammonia washers is preferably concentrated to an ammonia strength of 25% before despatch to a central chemical works for sulphate production.[195, 196] This concentration is normally carried out by stripping with steam in cast-iron stills having bubble-cap plates, but Raschig ring packing has also been used.[197] To obtain the required degree of concentration of the weak crude liquor, some form of dephlegmation of the excess of water vapour is required. Further, to prevent crystallization of the liquor at ambient temperatures and blockages in the final condenser, the carbon

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dioxide to ammonia ratio must not exceed a certain value. This process is known as decarbonation and the critical compositions of liquors have been determined experimentally.[198–200] Many plants and types of plants have been described and their relative merits discussed. Recent developments have been reviewed by Bell[201–203] from both the technical and economic aspects and plants have been classified as follows: (*a*) with internal or external dephlegmation, (*b*) having vapour phase or liquid phase decarbonation, and (*c*) with or without recovery of fixed ammonia. Internal dephlegmation is achieved by introducing cold feed to the top plate of the still, the alternative being a partial condenser external to the still. Vapour phase decarbonation is based on the fact that the initial rate of absorption in the condensed water vapour is greater for ammonia than for carbon dioxide. By arresting the condensation at a certain stage and separating the vapour and condensate, the absorption of carbon dioxide is minimized. Liquid phase decarbonation depends on the preferential desorption of carbon dioxide when the liquor is heated, any ammonia evolved being washed out with an unheated fraction of the feed. Methods for controlling the steam supply to the decarbonator have been given.[204, 205] Economic advantages are claimed for vapour phase decarbonation,[206] but the efficiency is limited to about 30%.[201] A comparison based on experience with both types of plant is reported.[207] Dissociation of the compounds formed by ammonia with the acid constituents of the liquor is almost complete above 100°. The liquor boils below this temperature, so pressure decarbonation has been strongly advocated.[208–212]

RECOVERY OF AMMONIA

Fixed ammonia may be recovered by adding lime slurry to the liquor after the acid constituents have been removed. The economics of the recovery depend on the costs of steam and lime.[213, 214] The need to add the lime as a thin slurry dilutes the liquor and affects the heat load,[215] but this can be offset to some extent by using still effluent to make up the slurry.[216] Alternatives to pure lime have been suggested in the form of dolomitic lime,[217] alkaline earth carbonates and zinc carbonate under pressure.[218] In some circumstances ammonium chloride and other fixed salts are recovered from the stripped liquor by evaporation.[219–221] In the ammonia recovery process, steam is normally passed directly into the base of the stripping still and dilution of the effluent occurs. This is a disadvantage where the effluent is recycled, as in the cyclic process described previously, and the use of indirect steam has been recommended.[222] Several methods have been described for utilizing waste heat to improve the economics of the recovery process,[223–226] but heat exchange between the crude liquor and the final effluent is favoured, since the latter has to be cooled where it is discharged to sewers.[200] The theory of the distillation of ammoniacal liquor[227] has not been developed as for ammonia washing, presumably because of the difficulty of obtaining equilibrium data for the system at the boiling point. It has been shown, however, that the partial pressure of ammonia over dilute aqueous solutions at 100° varies linearly with the pH value.[228] Also the partial pressures of ammonia, carbon dioxide and water vapour have been determined over solutions with a composition corresponding to ammonium carbonate or carbamate.[229, 230] By whichever method ammonia is recovered, most of it is converted into ammonium sulphate in a saturator. Various types of saturator have been described[231] and their design and operating features discussed.[232] The system sulphuric acid–ammonium sulphate–water has been studied in this connection.[233]

Simultaneous Recovery of Ammonia and Sulphur

Instead of neutralizing the ammonia in fuel gases with sulphuric acid manufactured in a separate plant, many processes have been devised for recovering the ammonia and sulphur in the gas simultaneously, mainly stemming from the work of such pioneers as Hills,[234] Claus,[235] Feld[236] and Burkheiser.[237] The processes of Hills and of Claus used the ammoniacal liquor obtained from the washing and cooling of gas to remove hydrogen sulphide. Such processes were reviewed in 1930 by the British Gas Industry[238] and were considered unlikely to replace oxide purification since they were more expensive, there was an appreciable ammonia loss, they required very careful operation and control and provided no outlet for the by-product ammonia.

Of the four processes of Feld,[239] the last two recovered the ammonia and hydrogen sulphide as ammonium sulphate and sulphur. Metal thionates were employed initially, but the addition of a metal was considered to be unnecessary and the final process used ammonium polythionates.[240] Overdick[241–244] modified the process to utilize the fact that the reaction between hydrogen sulphide and ammonium tetrathionate proceeds more rapidly in the presence of ammonia and he listed some of the reactions involved:

$$\begin{aligned}
&(NH_4)_2S_4O_6 + 2NH_3 + H_2S \rightarrow 2(NH_4)_2S_2O_3 + S\\
&(NH_4)_2S_4O_6 + 2NH_3 + H_2O \rightarrow (NH_4)_2S_2O_3 + (NH_4)_2SO_4 + S\\
&(NH_4)_2S_4O_6 + 3H_2S \rightarrow (NH_4)_2S_2O_3 + 5S + 3H_2O\\
&(NH_4)_2S_4O_6 \text{ (hot)} \rightarrow (NH_4)_2SO_4 + SO_2 + 2S\\
\text{or } &(NH_4)_2S_4O_6 + 2(NH_4)_2S_2O_3 \rightarrow 3(NH_4)_2SO_4 + 5S
\end{aligned}$$

The thiosulphate is regenerated by the absorption of sulphur dioxide:

$$2(NH_4)_2S_2O_3 + 3SO_2 \rightarrow (NH_4)_2S_3O_6 + (NH_4)_2S_4O_6$$

Certain aspects of the polythionate process such as temperature effect, ammonia to hydrogen sulphide ratio and the advantage and disadvantage of metal ions, have been considered[245] and a study has been made of the decomposition of the ammonia solutions under pressure into sulphate and sulphur.[246]

The final form of the Burkheiser process[247–250] employs a suspension of ferric oxide in dilute ammonia solution to remove simultaneously hydrogen sulphide, ammonia and hydrogen cyanide. The iron sulphide is filtered off and oxidized to give free sulphur, which is then extracted with ammonium sulphide. The sulphur is recovered by heating and oxidized to sulphur dioxide, which is scrubbed out with an ammonia solution to form ammonium sulphite. The sulphite slowly oxidizes to the sulphate on standing.

A further advance in the simultaneous recovery of sulphur and ammonia was the introduction by Bähr[251] of catalytic oxidation in the gas phase of hydrogen sulphide to sulphur dioxide required for the formation of sulphite. The most effective catalysts are those based on a combination of two metals, one of which is readily converted to the sulphide, the other being an oxygen carrier. Complete conversion and minimum loss of hydrogen are favoured by high space velocities and a temperature of 750°F. It was originally proposed to recover the sulphite as solid, partly by cooling and partly by electrostatic precipitation.[252–254] Later patents[255–257] refer to absorption of the gases in ammonium sulphite–bisulphite solutions, the final development being the 'Katasulf' process.[258, 259]

With the proposal by Hansen[260] to absorb hydrogen sulphide in ammonium sulphite–bisulphite solutions, the slow oxidation step of the Burkheiser process was replaced by the thionate decomposition step of the Feld process to produce ammonium sulphate and sulphur. Subsequently many patents were taken out on various aspects of the use of sulphite–bisulphite and ammonium and metal thionate solutions, principally by Hansen,[261–271] Bähr,[272] Bönnermann,[273] I. G. Farbenindustrie-A-G.[274–288] and Heinrich Koppers, A. G.[289–296] The Koppers C.A.S. process,[297, 298] which was of this nature, was abandoned because of severe corrosion difficulties, but it has recently been reconsidered with special reference to manganese thionate.[299, 300] Proposals for using compressed air to oxidize ammonium sulphite[301, 302] and to provide an alternative source of sulphur dioxide[303] have been made. Another member of this group of processes is that of the Gesellschaft für Kohlentechnik[259, 304–306] in which the thiosulphate is decomposed by heating with sulphuric acid:

$$3(NH_4)_2S_2O_3 + H_2SO_4 \rightarrow 3(NH_4)_2SO_4 + 4S + H_2O$$

Thus the quantity of sulphuric acid imported into the process is only one-third of that required for the neutralization of the ammonia. Although not strictly in this category, since ammonia is only removed by side reactions, the Perox process[307–309] employs an organic oxygen carrier to oxidize hydrogen sulphide to sulphur. The carrier, such as hydroxybenzene, is dissolved in ammonium thiosulphate solution, a portion of which is continuously bled off to remove thiocyanate and the excess of thiosulphate formed. Since the removal of sulphur and circulating liquor both involve loss of the catalyst, the side reactions should be kept to a minimum. A process whereby hydrogen sulphide precipitated zinc sulphide from ammoniacal zinc sulphate was proposed by Cobb,[310, 311] but conversion of the sulphide to sulphate proved too slow for the process to be economic. A parallel process based on copper sulphate[312] also involved roasting of the sulphide to the oxide, which was then redissolved in sulphuric acid. Similarly, ferrous sulphate solutions, such as pickle liquor, have been proposed for the simultaneous removal of sulphur, cyanide and ammonia.[313–316] Processes originally proposed for the recovery of ammonia and hydrogen sulphide by water-washing alone never became established because of the carbon dioxide present in coke-oven and coal gas; this competes with the hydrogen sulphide for ammonia.[317] Ammonia is not as selective as soda and potash for the removal of hydrogen sulphide in the presence of carbon dioxide,[318] but an appreciable measure of selective absorption is possible if the period of contact between gas and liquid is short.[319, 320] Appreciation of this fact led to the revival of the use of ammonia solutions for gas purification.[321–328] As the ratio of ammonia to hydrogen sulphide in the crude gas is rarely sufficiently high, ammonia must be recycled to the washing stage. It can either be recycled in the gas phase, as in the Pauling and Deutsche Geratebau process,[329] or in the liquid phase as in the Collin process.[330–333] In general these processes recover ammonia and sulphur separately, but a proposal has been made recently[334] to oxidize ammoniacal liquor catalytically under pressure to give a solution of ammonium sulphate.

A novel process proposed by Tern[335, 336] involved stripping ammonia from ammoniacal liquor and producing sulphur dioxide by burning sulphur recovered in the purifiers. The two gases were then ionized by high tension electric currents and brought together to form fertilizers. In the Staatsmijnen–Otto process[337] and the I.C.I. Auto process,[338] ammonia acts as an intermediary, sulphur being recovered in the elemental state. The latter uses iron salts only, while the former is based on potassium ferric-ferrocyanide.

$$2\text{KFe}[\text{Fe(CN)}_6] + 2\text{NH}_3 + \text{H}_2\text{S} \rightarrow 2\text{K(NH}_4)\text{Fe}[\text{Fe(CN)}_6] + \text{S}$$

$$2\text{K(NH}_4)\text{Fe}[\text{Fe(CN)}_6] + \tfrac{1}{2}\text{O}_2 \rightarrow 2\text{KFe}[\text{Fe(CN)}_6] + 2\text{NH}_3 + \text{H}_2\text{O}$$

Another sulphate that has been employed in an attempt to recover ammonia more economically is that of calcium. Gypsum has been used to recover ammonium sulphate from fully carbonated liquor.[339] Ammonia has been removed from gas, though not completely, by solutions or suspensions of calcium sulphate.[339–342] Parrish[343] reviewed the process for manufacturing ammonium sulphate from anhydrite, pointing out the many unit processes involved and discussing such practical problems as utilization of flue gas as a source of carbon dioxide, grinding the anhydrite, the slow nature of the reaction, separation of the calcium carbonate sludge and evaporation of the sulphate solution.

Recovery of Ammonia as Phosphate and Bicarbonate

Suggestions have been made for recovering ammonia otherwise than as the sulphate. The alternative forms most seriously considered are the phosphate and the bicarbonate. Several patents[344–348] describe the absorption of ammonia by acidified phosphate rock to form fertilizers. The recovery of ammonia as bicarbonate was thoroughly investigated by the British Gas Industry in 1930 and more recently in Germany.[349] The conditions necessary for solid ammonium bicarbonate to exist in equilibrium with ammonia and carbon dioxide in the gas phase are given[350] approximately by

$$p_{\mathrm{NH_3}} \times p_{\mathrm{CO_2}} = K_2$$

where $K_2 = 180$ mm. at 20°C. and 29·5 mm. at 10°C. Methods for achieving the necessary concentrations in the gas phase or in solution have been given by Parrish,[351] who proposed carbonating ammoniacal liquor with producer gas, and by Key, who patented two processes employing the carbon dioxide in the crude gas exclusively. The first process[352] achieved the necessary concentration of ammonia in the gas phase by concentrating all the free ammonia into one-third of the crude gas. This fraction of the gas was recycled after contact with a saturated ammonium bicarbonate solution. The second process[353] was based on decarbonating ammoniacal liquor to the point where the ratio of ammonia to carbon dioxide in the stripped vapours was that required to produce the bicarbonate on contacting the vapours with a saturated solution of the salt. In this method the decarbonated liquor was recycled. Increased pressure and reduced temperature favour the formation of bicarbonate and this is the basis of a German process.[354] In processes where hydrogen sulphide is scrubbed from gases by ammoniacal liquor, ammonium carbonate and bicarbonate are possible end products.[355, 356] Recovery of ammonia as the bicarbonate is economically sound only if it is comparable with ammonium sulphate as a fertilizer. From a series of trials it has been concluded that the large-scale use of ammonium bicarbonate as a fertilizer would require modification of the usual method of applying fertilizers to the soil.[357]

Excellent summaries of the foregoing conventional methods of ammonia recovery with extensive bibliographies are given in three textbooks.[358–360] In addition a number of reviews have been published of the processes available.[361–371] Where it is desired to restrict the absorption of the weak acid gases simultaneously with the ammonia, washing with a weak organic acid solution is recommended.[372–374] Alternatively an aqueous solution of a salt formed from a weak organic base and sulphuric acid is recommended.[375] The base, such as quinoline, should be insoluble in water and have a boiling point of at least 200°. Other methods proposed for the recovery of ammonia are: absorption in aqueous solutions of salts of the alkalis or alkaline earths[376–378]; absorption in wash oils commonly used for benzene extraction[379] or in high boiling alcohols[380]; passage through a bed of vanadic acid in the presence of water at 30–80° [381] or passage over fossilized vegetable matter such as peat at 200–500°.[382] In all except the last case ammonia is recovered by heating the absorbent. If water vapour is removed from coke-oven gas by cooling to 0°, ammonia and hydrogen sulphide may be separated out as the sulphide[383] by further cooling or as the hydrosulphide by heating to 40–50°.[384] The application of refrigeration to gas for the increased recovery of ammonia and other volatile by-products has been discussed by other workers.[385–391]

Recovery of Ammonia by Ion-Exchange

Another method for recovering ammonia, particularly from dilute mixtures, is by ion exchange. A French patent[392] in 1928 specifies the use of permutite for fixing ammonium ions in the solid state, and an American patent[393] ten years later involves the use of water-insoluble resins such as the condensation products of a polyhydric phenol and formaldehyde. The method is given as one of three for removing ammonia from boiler feed-water.[394] In recent years the method appears to have been widely adopted in Japan for concentrating ammonia wastes. The different regenerants proposed for the cation exchanger include boric acid[395] and ammonium dihydrogen phosphate,[396] both of which may be recovered by heating the resulting ammonium compounds. Sea water may be used to liberate the ammonia which may then be recovered by liming.[397, 398] Ion exchange resins are particularly suitable for separating substances having different degrees of ionization.[399] A method by which the ammonia is recovered as gas or in highly concentrated solutions employs electrodialysis to regenerate the cation exchanger.[400] Ammonia itself is a regenerant for the anion exchange material used in the purification of sugar-beet juice.[401, 42] It is recovered by distillation in the presence of a small quantity of lime.

Corrosion of Ammonia Recovery Plant

Much of the plant and equipment used for the recovery of ammonia from fuel gases is subject to corrosion unless special materials are used and adequate precautions taken. The thionate processes for the simultaneous recovery of ammonia and sulphur were beset by corrosion problems, and aluminium and its alloys were proposed as the materials of construction.[403] Replacement of steel tanks by concrete tanks for the storage of ammoniacal liquor has been recommended.[404, 405] Ammonium thiocyanate is considered to be the most corrosive constituent present in ammonium sulphate saturators, and this can be decomposed periodically by increasing the acidity to 20% for 1–2 hours.[406] Similarly, excessive corrosion of a deacidifier was found to be due to the presence of hydrogen cyanide.[407] Stainless steel is now widely used for the ancillary equipment in ammonia liquor concentration plants[408] and is recommended for all plant in contact with ammonium sulphate crystals.[409] Experience in the corrosion of aluminium and aluminium alloy condenser tubes on concentrated liquor plants has been described.[410]

Production of Pure Ammonia

If pure ammonia is required, either as a final product or as an intermediary, the crude ammoniacal liquor or vapours must be subjected to one or more purification processes. The percentage of the acid gases, carbon dioxide and hydrogen sulphide, may be reduced by an extension[411, 412] of the pressure decarbonation or deacidification step previously referred to.[208–212] Ammonia can be recovered free from these acid gases by distilling the crude liquor in two stages. When the acid gases have been substantially removed, lime is added and the residual free ammonia and all the fixed ammonia are recovered separately.[413] Washing of the ammonia vapours with milk of lime has also been proposed.[414] Recovery from the mixed vapours may be effected by washing with a reagent in which the acid gases are substantially insoluble and from which the ammonia may be recovered by simple heating. The solutions that have been recommended include those of calcium chloride,[415] ammonium thiocyanate,[416] salts of weak organic acids,[417–419] ammonium dichromate[420] and ammonium dihydrogen phosphate.[421] Combination of the liming and selective absorption processes has also been suggested.[422, 423] Removal of the acid constituents in combination with part of the ammonia is achieved by freezing out the appropriate compounds.[424, 425] Hydrogen sulphide alone may be oxidized to a non-volatile compound with or without catalysts,[426–428] or caused to react with a suspension of an iron ore or ferrous hydroxide.[430] Organic impurities may be precipitated from the crude liquor,[431] catalytically oxidized in the vapour phase[432, 433] or adsorbed by active charcoal.[434] Contamination of the ammoniacal liquor with higher tar acids may be prevented by complete tar removal from the hot gas.[435] Segregation of the fixed and free ammonia liquors is also advised.[436, 194] Two further methods of obtaining pure ammonia from the mixture with acid gases are by alkaline hydrolysis[437] or by absorption in acidified ammonium sulphate which is then electrolysed using a platinum anode and a mercury cathode.[438] To obtain anhydrous liquid ammonia, the gas is expelled under pressure from the solution in water[439, 440] or some other suitable absorbent.[441]

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SECTION V

THE SYNTHETIC PRODUCTION OF AMMONIA FROM ITS ELEMENTS

BY G. H. PAYN

The industrial synthetic preparation of ammonia has remained basically unchanged since its foundation by Haber in the early part of the twentieth century (Mellor, VIII, 158). Major variations of the process have been largely concerned with the use of different synthesis pressures. Haber himself has described his process in a Nobel Prize address.[1] The Haber–Bosch process uses synthesis pressures of 200–350 atm. A modern American plant[2] and several older plants employing the classical German process[3–8] are described in the literature. The Fauser process uses pressures similar to those employed in the Haber–Bosch process, but differs in details of technology.[9–11] The Claude process operates at pressures of 900–1000 atm. As a result higher conversion of reactant gases to ammonia occurs in a single pass over the catalyst, compared with yields in the lower pressure syntheses; liquefied ammonia is more readily separated from the reactant gases without resort to refrigeration, and purification of the reactants is easier.[12] Claude himself describes the development of his process[13] and various devices for removing the heat of reaction are specified in his patents.[14–17] Descriptions of modern plants using Claude's process have been published.[18, 19] The Casale process also operates at high pressures —normally about 750 atm.[20–22] At the other end of the scale the Mont Cenis process, which employs pressures of about 100 atm., was developed in Germany essentially as a means of avoiding the original Haber patents.[23, 24] In a comparison of the various processes[25] it is stated that, in 1952, 70% of the synthetic ammonia produced in America was synthesized by plants operating at pressures between 100 and 350 atm. Fig. 1 shows a typical flow diagram of a plant making ammonia from natural gas. The plant concerned actually operates the Claude process, but the flow diagram is equally applicable to the other processes described.

The synthesis of ammonia from air and water is described in a number of patents. Iron, its oxides and hydroxides, and nickel are stated to catalyse the reaction.[26] Alternatively, the gases are caused to react over carbon at 800°C.[27, 28] or over a mixture of bentonite and carbon.[29, 30] As far as is known none of these processes is used commercially.

Sources of Nitrogen and Hydrogen

Nitrogen for ammonia synthesis is normally obtained directly from the atmosphere. A large variety of methods, however, is used for producing hydrogen. The original German plants operating the Haber process used water-gas or producer gas from suitable indigenous fuels, and many plants still operate with these raw materials. Hydrogen sulphide is removed from the gases at low temperature by iron oxide, and the partially purified gas is caused to react with steam over an iron catalyst, giving the well-known shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

thus producing further hydrogen.[31–33]

The Claude process (see above) for ammonia synthesis was developed in conjunction with Claude's separation of the constituents of coke-oven gas by liquefaction.[34] The Linde process for gas separation is also used, and the two processes

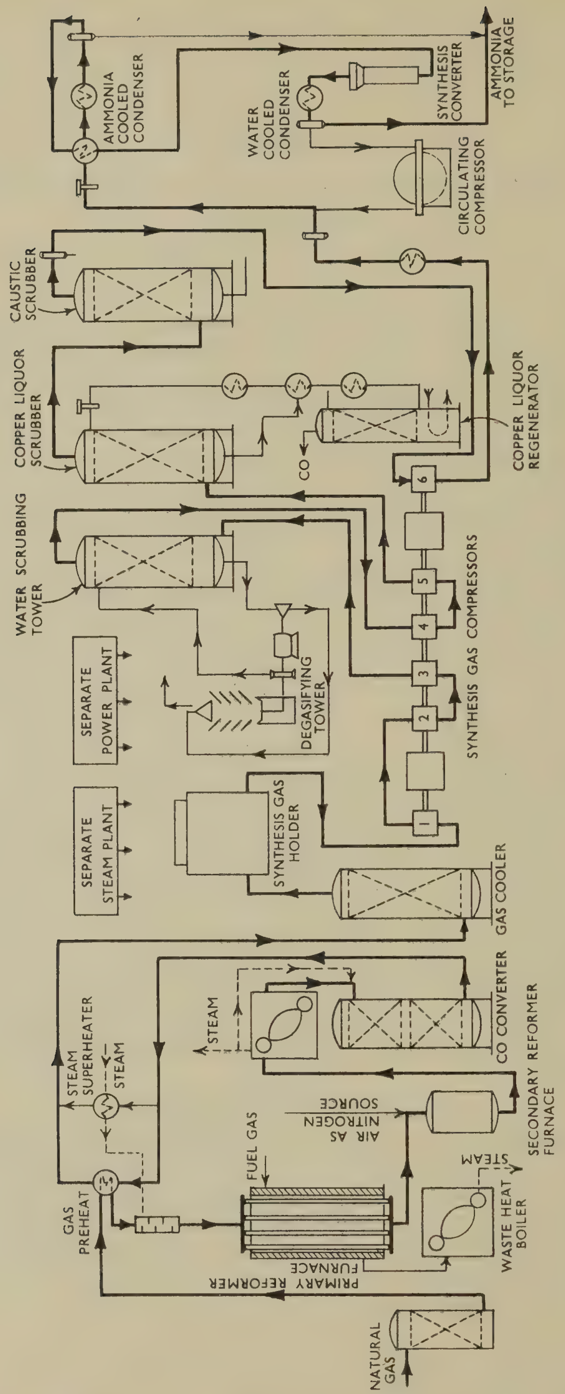


FIG. 1.—Production of ammonia from natural gas; flow diagram

have been contrasted.[35] Synthesis gas may also be prepared from coke-oven gas by cracking in the presence of oxygen and steam at high temperatures.[36] The possibility of using blast-furnace gas, by enrichment of the blast with oxygen or by adding steam to react with carbon monoxide, has been widely discussed.[37–40]

Hydrogen from the electrolysis of water is used where electricity is cheap, or the hydrogen may be a by-product of some other industry.[41] The Fauser process (see above) is normally connected with the use of Fauser electrolytic cells.[42]

Hydrogen for ammonia synthesis is being more and more commonly produced by the thermal decomposition, reforming or oxidation of hydrocarbon gases. The reaction of methane with steam over an iron or nickel catalyst,

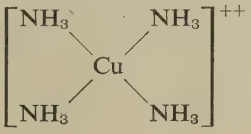
$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

is well known, and it is stated that a gas containing 77% of hydrogen and 12% of carbon monoxide can be made by this method; the carbon monoxide then further reacts with steam by the shift reaction (see above). Thermal decomposition is said not to be an economic proposition for making ammonia synthesis gas.[43, 44] Partial oxidation of hydrocarbons at high pressure and temperature (1100°C.) is another source of hydrogen and carbon monoxide, and again the gas undergoes a subsequent shift reaction.[45] If the oxygen is replaced by oxygen-enriched air, the mixture is directly suitable for ammonia synthesis.[46] The possible use of natural gas for ammonia synthesis was forecast in 1929[47] in a paper setting forth the thermodynamic equations, whilst a plant using the reforming of natural gas to obtain hydrogen for ammonia was described in 1932.[48] Since the 1939–1945 war, ammonia production has been associated with the development of the petrochemical industry and the utilization of natural gas in America,[49] France,[50, 51] and Italy.[52]

Solid fuels other than coke are used for hydrogen production; the material used depends very much on the natural resources of the country concerned. Gasification of low grade coals with steam is described in patents and technical papers from Japan,[53] Russia,[54–57] Italy,[58, 59] and Sweden.[60] Wood gasification is employed in an Indian synthetic ammonia plant.[61] Synthetic ammonia is made also from gases produced as by-products in the fermentation of corn[62, 63] and from tail gases from nitric acid manufacture.[64]

Purification of the Gases

When carbonaceous materials are gasified to provide a source of hydrogen, extensive purification of gas must follow. The normal contaminants in the gas are oxides of carbon, hydrogen sulphide and organic sulphur compounds, including thiophen, carbonyl sulphide and mecaptans. Hydrogen sulphide is removed in an early stage of purification by iron oxide in processes similar to those used for purifying town's gas. The desulphurized gas passes through the catalysed shift reaction (see above) and is subsequently purified from other contaminants. Carbon dioxide is frequently removed by scrubbing the gases with water at pressures between 10 and 50 atm., 25 atm. being commonly used.[65] The addition of ammonium nitrate or sulphate to the scrubbing water is said to increase the efficiency of carbon dioxide removal by 4–5%.[66] Residual hydrogen sulphide is removed by the water scrubbing. Organic bases, notably the ethanolamines, are also used commercially for removing carbon dioxide and hydrogen sulphide from synthesis gases.[67, 68] Carbon monoxide which has not been converted during the shift reaction is normally removed by scrubbing the gases at pressures between 100 and 250 atm. with an ammoniacal solution of a cuprous salt. Cuprous carbonate, formate or acetate is commonly used. It is stated that the cuprous complex



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has no activity in carbon monoxide removal. The activity of the cuprous complex depends largely upon the concentration of 'free' ammonia (i.e. ammonia in excess of the stoicheiometric requirements of the anions in solution), as the addition of ammonia permits the co-ordination of more molecules of carbon monoxide.[69]

In the Claude and Linde processes for purification of coke-oven gas, the mixed gas is liquefied either by the Joule–Thomson effect (Linde) or by compressing the gas and allowing it to do external work in a heat engine (Claude).[70] In the final separation, liquid nitrogen removes carbon monoxide, hydrocarbons and sulphur compounds.[71] The Linde process has advantages over the Claude process,[73] and both of them are described in the literature.[72–74] The Claude process also uses a catalyst to convert traces of carbon monoxide to methane and water,[75] and similar catalytic purification is described by other workers for removing oxygen-containing compounds.[76–78]

Final removal of organic sulphur compounds is frequently carried out by the use of active charcoal and, according to the patent literature, the presence of water vapour[79] or alkali[80] is advantageous. The capacity of charcoal for removing hydrogen sulphide from ammonia synthesis gas has been measured.[81] Washing the reactant gases with liquefied ammonia at a late stage in the purification process is also claimed to remove traces of catalyst poisons such as water, hydrogen sulphide, oxides of carbon and hydrocarbons.[82–85] Patents also claim the use of molten alkali metals,[86–89] alkali metal amides,[90, 91] alkali metal hydrides,[92] solutions of alkali or alkaline-earth metals in liquefied ammonia[93–95] or solutions of inorganic salts in liquefied ammonia[96, 97] for final synthesis gas purification, but as far as is known none of these processes is used commercially.

REMOVAL OF INERT GASES

As air is normally the source of nitrogen for synthetic ammonia manufacture, the nitrogen is accompanied by inert gases which must be removed at some stage of the process. Unless a liquefaction process is used to purify the nitrogen, the inert gases find their way to the final ammonia synthesis reactors, where they tend to concentrate as nitrogen and hydrogen react to form ammonia and the ammonia is removed. The effect of these diluent gases on the rate of reaction has been calculated[98]; at lower pressures (200 atm.) the ammonia concentration at equilibrium decreases as the square of the concentration of inert gas, whilst at higher pressures it decreases directly with the concentration of inerts. The tolerable concentration is decided by economic considerations. To maintain this concentration, a portion of the gas in circulation must be purged periodically or continuously; as the purged gas is richer in inert gases than the atmosphere, it forms an excellent source for their separation.[99] Various methods of recovering argon, krypton and xenon are described in patents, e.g. by liquefaction and distillation, with[100] or without[101, 102] prior chemical treatment, or by extraction of the gases with liquid hydrocarbons, followed by rectification,[103–105] a process that is particularly useful for separating krypton and xenon.

The purification of gases for ammonia synthesis is reviewed in an article concerned with general industrial gas purification.[106]

Equilibrium Conditions

The equilibria data for ammonia in contact with a 3:1 hydrogen:nitrogen mixture, measured by Haber and Le Rossignol and by Larson and co-workers (Mellor, VIII, 156) have not been supplanted. The effects of temperature and pressure have been separated in analyses by later workers[107] whilst extrapolation from the experimental results is made easy by a nomogram.[108] Equilibria constants at high pressures can be calculated from the lower pressure measurements and activity coefficients.[109, 110]

The heat of formation of ammonia at various temperatures and pressures has been calculated using a modified form of the Beattie–Bridgman equation of state.[111] Other authors challenge the validity of these calculations, and substitute slightly different constants which allow for the heat of mixing of the components of the system.[112]

The kinetics of the synthesis and decomposition of ammonia over iron catalysts has been investigated by many workers, notably in Russia. Earlier equations for the rate of formation[113] (Mellor, VIII, 157) have been supplanted by the generally accepted equation of Temkin and Pyzhev. These workers measured the rate of formation of ammonia over potash/alumina promoted catalysts at temperatures of 400–450°C. and at atmospheric pressure. They state that the rate-determining factor in the forward reaction is the activated adsorption on the nitrogen-free surface, while for the reverse (decomposition) reaction, the rate of ammonia desorption is the determining factor. The equation

$$\frac{dp_{NH_3}}{dt} = k_1\frac{(p_{N_2}p_{H_2})^{1\cdot5}}{p_{NH_3}} - k_2\frac{(p_{NH_3})}{p_{H_2}{}^{1\cdot5}}$$

is shown to fit the experimental data.[114, 115] Temkin and Pyzhev's experimental results were confirmed by other workers for a similar catalyst[116, 117] but do not apply to an iron catalyst promoted with alumina only; this apparent discrepancy was later explained.[118] Molybdenum,[119] tungsten[120] and supported ruthenium catalysts[121] were also studied by the Russian workers. The results for molybdenum and tungsten fitted the Temkin–Pyzhev equation well, but modifications had to be made for ruthenium, in which case the activated adsorption of hydrogen is stated to be important. The apparent activation energy of decomposition was between 42,000 and 45,000 g.-cal./mole for iron and molybdenum catalysts, but 59,250 g.-cal./mole for ruthenium. It is calculated as 46,500 g.-cal./mole by Temkin[122] and shown to be in good agreement with the experimental results of the author and other workers.[123] The Temkin–Pyzhev equation is extended to higher pressures, taking into account departure from ideal gas conditions.[124] Kinetic equations are also derived *inter alia* for ammonia synthesis and compared with the results of other authors[125]; this paper also tabulates equilibrium data for pressures between 1 and 1000 atm. and from 200° to 740°C.

As the synthesis of ammonia is an exothermic reaction, the lower is the temperature at which synthesis can be conducted, the higher is the equilibrium yield (Mellor, VIII, 155). If the reactant gases are passed through an uncooled catalyst mass, the temperature of the gases rises, owing to the heat of reaction. As the temperature rises, the equilibrium condition becomes less favourable for ammonia formation until, in the limit, decomposition balances formation, and the temperature ceases to rise. Various devices have been employed, therefore, to remove the heat of reaction progressively or step-wise so that equilibrium conditions favouring synthesis are maintained throughout the catalyst mass. The cooling medium may be the incoming gas passing through tubes embedded in the catalyst mass.[126–128] (Fig. 2), or surrounding the catalyst container.[129–132] Alternatively the gas may be quenched at intervals through the catalyst bed by injection of cold reactant gas[133–135] (Fig. 3). In the Fauser converter (*v.s.*)[136] (Fig. 4) the catalyst is cooled and steam raised by passing water through tubes in the catalyst mass. Fig. 4 also shows the temperature profile and the increase of ammonia concentration through the catalyst bed. Coolants other than water have been described.[137] With a knowledge of the rate of reaction under prevailing conditions, frequently calculated by Temkin and Pyzhev's equation [*v.s.*] and of the equilibrium conditions, the optimum temperature profile through a catalyst bed may be calculated. For more detail, the reader is referred to an excellent mathematical handling of the problem[138] and to many other publications on the subject.[139–143]

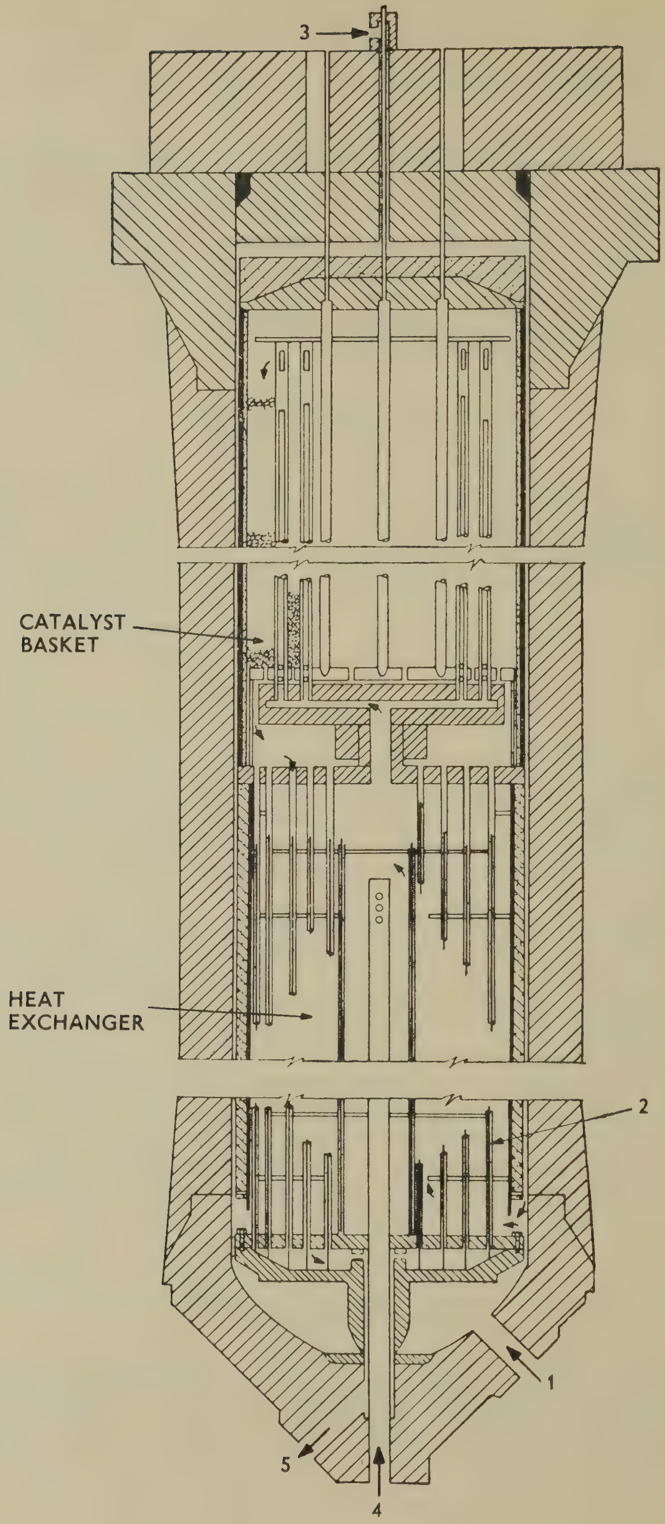

Fig. 2.—Synthetic production of ammonia: cooling system

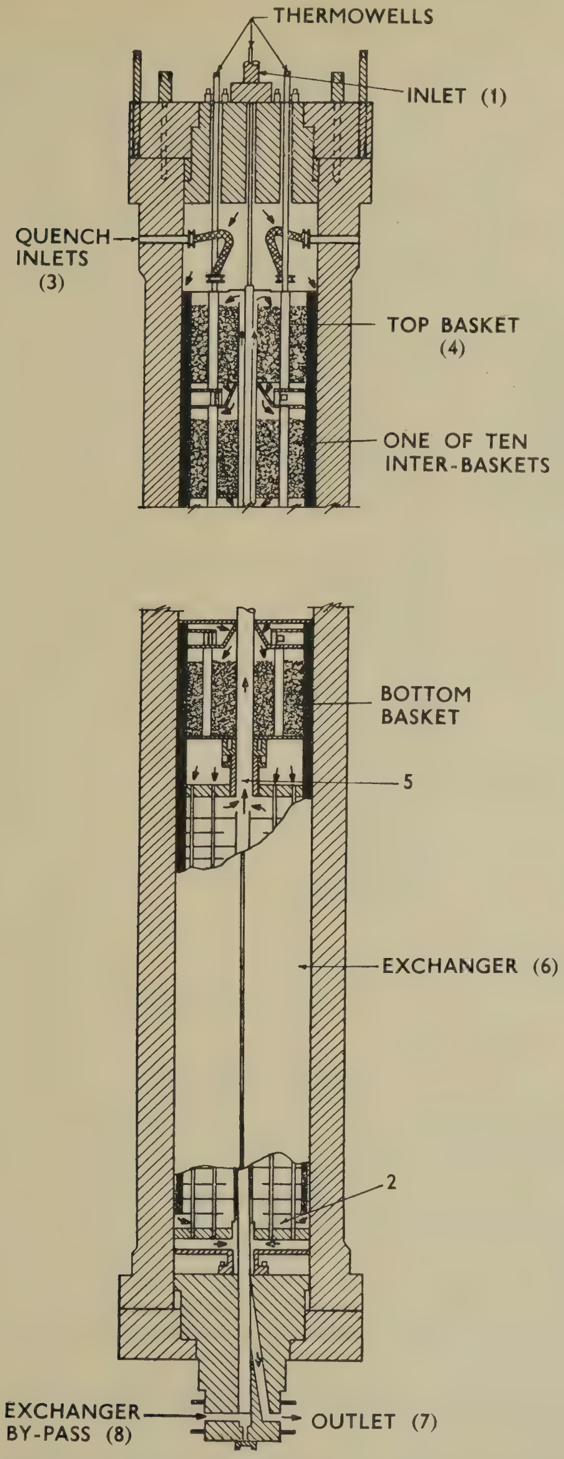

FIG. 3.—Synthetic production of ammonia. Injection of cold reactant gas

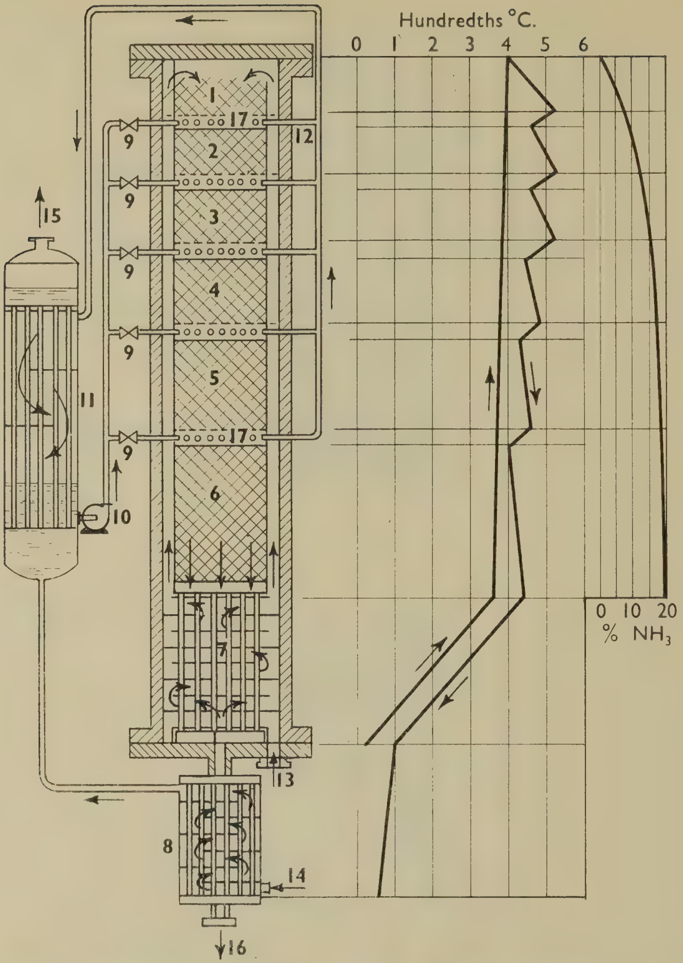

FIG. 4.—Fauser converter: temperature profile and ammonia concentration increase through catalyst bed

Catalysts and Promoters

Iron is practically the only catalyst used commercially for ammonia synthesis. It is rarely used, however, without the addition of promoters; an unpromoted catalyst made by repeatedly oxidizing with steam and then reducing the α-iron prepared from magnetite has been described.[144] Oxides of iron are commonly fused or sintered with promoters. Mixtures of potash and alumina varying between 1% and 3% Al_2O_3 with 0·7%–1% K_2O are very often used as promoters.[145, 146] The large-scale production of such a catalyst has been described.[147] Potassium is added as nitrate or carbonate, and the mixture may be heated in a stream of oxygen.[148, 149] A fluidized potash–alumina promoted iron oxide has been prepared.[150] Addition of magnesia and zirconia to potassium and aluminium promoters is stated to improve the catalyst.[151] Magnesia alone[152] or mixed with potash and silica also acts as a promoter,[153, 154] or an oxide of chromium may replace the silica.[155] A catalyst containing at least 25% of the promoters already mentioned is said to be of particular benefit in ammonia synthesis at pressures over 1000 atm.[156] Other oxide combinations claimed in patents to act as promoters are Li_2O-MgO, Na_2O-MgO, Na_2O-CaO,

K_2O-BaO,[157] and a mixture of 'difficultly reducible oxides of uranium, thorium and zirconium' to which has been added metallic calcium, aluminium or magnesium[158]; it is claimed that the oxides are partially reduced during the preparation of the catalyst by the added metals. Metallic aluminium alone has a promoting action on iron or on manganese.[159, 160] A fused catalyst containing potash and relatively high (10%) concentrations of silica is claimed to be highly active,[161] but this is contrary to the experience of most investigators (*vide infra*).

Naturally occurring ores of iron are frequently used for catalyst preparation. Hæmatite containing alumina (0·9%), silica (1·6%), ferrous oxide (0·53%) and calcium oxide (0·09%), together with traces of manganese, sulphur and phosphorus, has been used.[162] Natural magnetite with or without the addition of promoters is a satisfactory catalyst.[163, 164] It is desirable that magnetite ores should be treated by magnetic separation if their silica content is high.[165, 166] The lower silica content of artificially prepared magnetite is stated to account for its higher activity as a catalyst, compared with certain naturally occurring magnetites.[167] Titanomagnetite-based catalysts, however, are said not to be highly active, and to lose their activity very rapidly when exposed to oxygen or carbon monoxide.[168, 169] Siderite containing alumina, silica and magnesia is said to be a good catalyst without addition of further promoters.[170] In all fused iron catalysts, the highest activity is exhibited when the iron oxide used is in the form of Fe_3O_4; this observation has been made by many workers[171–173] (see also Mellor, VIII, 159).

In addition to the fused catalysts so far described, the patent literature contains a host of claims for precipitated iron catalysts based on complex cyanides. A recipe which appears frequently with various minor modifications is the precipitation of ferro- or ferri-cyanides of the alkali (potassium in particular) or alkaline-earth metals with aluminium salts.[174–176] It seems very probable that the complex salts, under the high-temperature reducing conditions of ammonia synthesis, are decomposed and reduced to metallic iron in which the minor constituents are evenly distributed as promoters. This theory was suggested by Mittasch and his co-workers,[177, 178] who advance the following view of the mechanism of reduction. Ammonium ferrocyanide and potassium aluminium ferrocyanide are said to decompose at high temperature in a nitrogen–hydrogen mixture with intermediate formation of a substance having the composition corresponding to $Fe(CN)_2$. Purely thermal decomposition of $Fe(CN)_2$ gives iron, carbon, Fe_3C and nitrides of iron and nitrogen. In nitrogen–hydrogen mixtures at 230°C. the carbon and nitrogen are reduced at the same rate, and the completed reaction yields iron. At 400°C. the rates of reaction differ, and iron, Fe_3C and carbon are formed, probably with FeC_2 as an intermediate; reduction can still proceed further. Other workers say[179] that catalysts produced from potassium aluminium ferrocyanide are most active at temperatures slightly below 400°C. and are then slightly more active than reduced titanomagnetite (which, however, is not considered a good catalyst, *vide supra*).

Molybdenum–iron mixed catalysts, with or without promoters, are also mentioned as being very active in ammonia synthesis. Binary mixtures of molybdenum with iron, nickel, cobalt, copper, chromium and tungsten have been investigated.[180] In all cases, a molybdenum content greater than 50% was required for the catalyst to maintain its activity over several weeks. It is recorded[181] that iron–molybdenum–alumina catalysts are less active than iron–alumina catalysts, although addition of alumina to iron–molybdenum catalysts maintains activity for longer periods. Catalysts which are active at low temperatures (177–316°C.) and pressures (1–70 atm.) can be made from sulphides of chromium, tungsten or molybdenum in admixture with the sulphide of a metal of the iron group.[182] Other catalysts claimed to be highly active at low temperatures and pressures are made from granular mixtures of iron, nickel or cobalt with magnesium or vanadium, to which copper may be added.[183, 184] Such a catalytic material supported on alumina, operating at a pressure of 75 atm. and at 290°C. is stated to give $2\frac{1}{2}$ times the yield of ammonia obtained from the classical Haber–Bosch process at 200 atm. and 500°C.[185]

Alkali or alkaline earth metals in vapour form are claimed to be promoters for iron catalysts.[186, 187] Compounds of arsenic, boron and phosphorus are stated to increase the activity of iron catalysts when added to the promoter,[188–190] although these substances are normally regarded as catalyst poisons. A catalyst composed of 84% of $(NH_4)_6Mo_7O_{24}$ and 16% of aluminium nitrate is said to be more active than a commercial catalyst at a much lower temperature.[191] Exposure of a standard catalyst in an inert atmosphere to high frequency radiations is said to increase its activity.[192] Subjecting the reactant gases to ultrasonic vibrations between 30,000 and 50,000 cycles per sec. using a fluidized iron catalyst is also claimed to give high yields of ammonia at low temperatures and pressures.[193]

Iron catalysts are poisoned by a variety of agents. Decomposition-products of machine oils cause poisoning, and it is reported that loss of activity is a function of penetration of the catalyst by the decomposition product; greater degrees of poisoning occur as pressure is increased.[194] Concentrations as low as 0·001% of hydrogen sulphide or phosphine in the reactant gases cause poisoning; the effect of poisoning is reduced by increase of temperature, but again increases with increasing pressure.[195] Temperature and pressure variations have similar effects when water vapour is the poison (cf. Mellor, VIII, 159), and less active catalysts are poisoned more readily.[196]

A number of authors claim that the conditions of reduction of the iron oxide have a considerable influence on the activity of the final catalyst; temperatures and pressures as low as possible, giving slow reduction, are preferable.[197–201] The catalysts in the reduced state are pyrophoric, and hence difficult and hazardous to handle; a number of workers have suggested means of stabilizing the catalyst by controlled oxidation which, it is claimed, gives a unimolecular oxide film over the catalyst. Water vapour or carbon dioxide may be used for this purpose,[202] but preferable methods are to use nitrogen–hydrogen mixtures containing a fraction of one per cent of oxygen,[203, 204] or to nitride the catalyst with dry ammonia.[205] A large-scale plant for catalyst stabilization, which apparently does not affect the activity of the finished catalyst, has been described.[206] Used or poisoned ammonia synthesis catalyst may be regenerated with air or steam[207] or by treatment with iron carbonyl, which when decomposed is said to form an active layer,[208] or by remelting alone[209] or after moistening with potassium nitrate solution.[210]

Reaction Mechanism

According to Frankenburger and his co-workers[211–216] the synthesis of ammonia on iron or tungsten catalysts proceeds in two steps. Nitride formation is followed by nitride hydrogenation to adsorbed NH or a metal imide. Further reaction with hydrogen forms adsorbed ammonia, which is then desorbed. The total activation energy of the two steps must be less than the activation energy of the uncatalysed reaction. For the second step to have a low activation energy, the metal nitride should have a low stability; this reasoning is applied to show why iron is a good catalyst whereas, for example, vanadium is not. Other authors support Frankenburger's work.[217]

Considerable attention has been given to the formation of nitrides on iron surfaces in connection with the synthesis of ammonia. From measurements of the decomposition of ammonia over a promoted iron catalyst, it is concluded[218] that nitride hinders the decomposition of ammonia, and that iron, not nitride, is the catalyst. The belief that the activated adsorption of nitrogen on the metal surface is the rate-determining step (mentioned by many workers) is expressed as a result of experimentally heating iron or nickel in the presence of hydrogen cyanide.[219] It is calculated[220] from measured heats of adsorption of nitrogen and hydrogen on an iron catalyst that 99·99996% of the catalyst surface is covered by nitrogen in ammonia synthesis. It is suggested that, in spite of the apparent lack of room for hydrogen on the catalyst surface, the reaction can occur by adsorption of nitrogen and hydrogen on different crystallographic sites, by solution of hydrogen in the metal or by decrease in the heats of adsorption as the coverage of the surface increases, thus bringing the values for hydrogen and nitrogen closer together; an energy diagram is proposed to show the heats of adsorption in various steps of the ammonia synthesis.

Investigations on the rôle of promoters have been largely confined to the potash–alumina promoted iron oxide catalysts. Alumina additions prevent crystal growth and hence reduction of active surface[221]; by the same argument, many promoters increase the stability of the catalyst towards heat,[222, 223] although excessive quantities of potash lower the activity of the catalyst. It is essential that the promoter should form a solid solution with the main body of the catalyst, as smaller crystals and a more porous product result.[224] Russian workers investigated the low temperature adsorption of hydrogen and nitrogen on promoted catalysts.[225, 226] One type of nitrogen sorption only was observed, but two types of activated hydrogen adsorption occurred at different temperatures. Emmett and Brunauer[227, 228] confirmed that two types of hydrogen chemisorption occurred, and later Emmett,[229] from work on the hydrogen–deuterium exchange at −195°C., postulates a third type of hydrogen chemisorption. Emmett and Brunauer also showed by measuring the low temperature chemisorption of carbon dioxide, carbon monoxide and oxygen that more than 50% of the surface of a catalyst containing 1% of K_2O was covered by the alkali and that alumina is also concentrated on the catalyst surface. Promoters may increase the catalytic surface by a factor of about 10, but it does not necessarily follow that the catalyst with the greatest surface area has the greatest activity—in fact a case is cited[230] where the converse applied. Emmett and his co-workers showed[231] that after thorough reduction, a standard iron catalyst retained sufficient hydrogen to cover 35% of the catalyst surface, even after prolonged outgassing; whether the hydrogen is chemisorbed by the iron or the alumina is not clear. Emmett's work has received the support of other workers.[232, 233]

For detailed information on catalysis in ammonia manufacture, the reader is referred to an excellent monograph with an extensive bibliography by Nielsen,[234] while several of the workers already mentioned contribute to a survey of catalysis including, *inter alia*, ammonia synthesis.[235]

Plant Materials

The development of high-pressure processes, of which ammonia synthesis was one of the earliest, has made great demands on the metallurgist. High pressures in themselves do not present a very great problem, but in conjunction with the high temperatures found in the synthesis reactors, they have made essential the development of special alloys. It is generally agreed that a steel of low carbon content (0·2–0·3%) is necessary, as the carbon is attacked and removed by hydrogen.[236–238] Chromium, nickel, tungsten, molybdenum and titanium are added to the steel to reduce attack by hydrogen and to prevent embrittlement and deformation at high temperatures (*loc. cit.*[239, 240]). According to one authority[241] deterioration of steels under the conditions of ammonia synthesis is caused primarily by hydrogen attack, followed by the formation of unstable nitrides; the presence of chromium is said to have a protective influence owing to the comparatively high stability of chromium nitride.

Originally, synthesis reactors were made from large seamless forgings, but modern techniques have permitted the use of welded[242] or steel-tape-reinforced vessels.[243] Data for various alloy steels of the types mentioned are given by Russian workers.[244–246]

Non-catalysed Synthesis

The formation of ammonia from its elements under non-catalytic conditions has been studied by a number of workers. Ammonia is formed from carefully purified nitrogen and hydrogen by the impact of slow electrons; this formation is considered not to be the result of a glow discharge, as ammonia is formed at potential differences less than the ionizing potentials of hydrogen and nitrogen.[247–249] Nevertheless, ammonia is formed in the glow discharge at pressures between 0·1 and 4 mm. The rate of formation of ammonia at these pressures is proportional to the current

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passing through the discharge tube. Dilution of the reactant bases (in stoicheiometric proportions) with hydrogen or argon decreases the rate of synthesis, although the presence of helium has no influence over a wide range of partial pressures. Small additions of nitrogen, however, increase the reaction rate, while large additions decrease it. The results are interpreted as showing that N_2^+ and N^+ ions initiate the reaction.[250–252] These suggestions are substantiated by the work of later investigators who showed that alkali ions activate the synthesis; the critical voltage required to initiate reaction varies with atomic weight of the alkali metal.[253, 254] The work has been summarized.[255] Other workers[256] have also demonstrated the presence of N_2^+ and N^+ ions, and measured the effect of frequency on ammonia formation in an electric arc.[257] The same workers investigated the simultaneous formation of ammonia and hydrogen cyanide in the electric arc from mixtures of hydrogen and nitrogen with carbon dioxide, or hydrocarbons.[258] Kunsman[259, 260] demonstrated the emission of positive ions from granules resembling standard ammonia catalysts and showed than an iron–potassium ion source was highly active while, even at much higher voltages, potassium ions alone had no effect. An explanation of the 'Kunsman source' is advanced by later workers.[261] Kunsman uses his apparatus to measure the relative activity of different ammonia catalysts.[262] Ammonia is formed from its elements in a high voltage discharge from a mercury electrode; increasing the mercury surface increased the formation of ammonia.[263] Other workers[264, 265] found that mercury vapour accelerated ammonia formation in the glow discharge, although zinc, cadmium and sodium vapours had negative effects.

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SECTION VI

THE PHYSICAL PROPERTIES OF AMMONIA

BY J. D. F. MARSH

STRUCTURE

Crystalline ammonia has a slightly deformed cubic close-packed structure, each nitrogen atom having six hydrogen atoms at a distance of 3·38 A., corresponding to six hydrogen bonds.[1] There are 4 molecules in the unit cell. At -185°C. $a=5·2253$ A. compared with $a=5·2153$ A. for ND_3.[2] The difference is attributed to zero point vibration, and the magnitude of the isotope effect indicates that the molecules do not rotate in the solid state at -185°C. Earlier determinations of the lattice constant were 5·08 A. at -170°C.,[3] 5·19 A. and 5·12 A. (Mellor, VIII, 173). The low dielectric constant of solid ammonia and its small temperature coefficient also show that there is little or no rotation in the solid.[4, 5] Measurement of the line width for nuclear magnetic resonance indicated, however, that hindered rotation occurred.[6] The molar volume of ammonia at 20°K. is 19·65 cm.[3, 7]

Gaseous ammonia has a pyramidal structure. Calculations from spectroscopic data give 1·014 A. for the N–H bond length and 106° 46′ for the H–N–H bond angle. Electron diffraction measurements give 1·015 A. and 106° 36′.[8] Force constants for stretching and vibration are also obtained from the spectroscopic data. The inversion barrier is about 6 kcal./mole.[9, 10] The following values of the bond dissociation energy have been calculated from published information: NH_2–H 104 ± 2, NH–H 88 ± 4, N–H 88 ± 2 kcal./mole.[11] The value of 104 kcal./mole for the dissociation energy of the first N–H bond in ammonia was confirmed by measurements of the rate of pyrolysis of N_2H_4.[12]

Modern theoretical treatment of the structure of ammonia is based on the application of wave mechanics (Partington, I, 377). Since a rigorous solution of the Schrödinger wave equation cannot be obtained, an approximation must be made, leading to an approach by either the molecular orbital or the linear combination of atomic orbitals. Various properties of the ammonia molecule, such as bond angles, bond energies and dipole moments, have been calculated and compared with the measured values.[13–38]

The structures of liquid and solid ammonia are influenced by the formation of hydrogen bonds. Thus Taft and Sisler calculated that if there were no hydrogen bonding the m.p. and b.p. would be 108°K. and 143°K. instead of the observed values of 195·4°K. and 239·7°K. The energy of the hydrogen bonds in the solid is 1·31 kcal./mole and 26% are broken on melting, 7% between the m.p. and b.p. and 67% on boiling.[39] Hellens calculated the cohesive energy of solid ammonia, taking account of the multipole forces as far as the dipole–octapole term.[40] Fyfe obtained 5·1 kcal./mole for the hydrogen bond energy of ammonia, and suggested that hydrogen bond formation depends on the presence of asymmetric lone pairs of electrons and reasonably short interatomic distances.[41] Other factors are the availability of suitable energy levels[42] and the partial charge on the hydrogen atoms, which is $+0·06$ v. for ammonia.[43]

VAPOUR DENSITY

From measurements of the mass of the normal litre of ammonia at various pressures below 1 atm. the limiting value at zero pressure has been obtained by linear extrapolation and used to calculate the mol. wt. of ammonia.[44–53] More recently it was pointed out that curvature of the plot of pv against p is significant,[54] and the best expression for L_p, the mass of the normal litre in g. at p atm. pressure, is:

$$L_p = 0{\cdot}759913 + 0{\cdot}011547p - 0{\cdot}0000061p^2$$

Comparison with the value for oxygen gives 17·0327 for the mol. wt. of ammonia and thus 14·0085 for the at. wt. of nitrogen.[55]

CRITICAL CONSTANTS, COMPRESSIBILITY AND EQUATIONS OF STATE

There have been no measurements of the critical constants of ammonia since those reported in Mellor, VIII, 183. The most reliable values are those given by Pickering in International Critical Tables: $T = 132{\cdot}4$°C., $P = 111{\cdot}5$ atm. and $V_c = 0{\cdot}235$ c.c./g. Kopper measured the critical temperatures of NH_3 and ND_3 and obtained 132·5°C. and 132·3°C. respectively.[56]

PVT measurements have been made at 30–200°C. and 100–1000 atm.,[57] at 50–325°C. and 15–130 atm.,[58] at 200–300°C. and 100–1629 atm.,[59] and at 50–150°C. and 1000–10,000 atm.[60] Some of these values for liquid ammonia are given in Table I, and for gaseous ammonia in Table II.

Table I.—Pressure–Volume Relation for Liquid Ammonia
Volume of liquid ammonia in c.c./g. at the following pressures in atm.

Temperature, °C.	100	200	500	1000
0	1·55	1·58	1·52	1·482
50	1·730	1·704	1·634	1·545
100	2·082	1·998	1·820	1·678
150	—	2·770	2·10	1·844
200	—	6·28	2·57	2·032

Table II.—Pressure–Volume Relation for Gaseous Ammonia
Pressure of gaseous ammonia (in atm.) and volume (in c.c./g.)

Temperature, °C.	95 atm.	70 atm.	40 atm.	20 atm.
100	17·36	22·84	36·47	58·28
150	20·18	21·81	44·11	76·24
200	22·93	30·64	51·29	92·57
300	28·29	38·08	65·03	123·10

These data have been fitted to a number of equations of state,[61–78] and the experimental values of the virial coefficients compared with calculated figures.[79–87]

VAPOUR PRESSURE, MELTING POINT, BOILING POINT AND LATENT HEAT

Overstreet and Giauque[88] related their measurements of the vapour pressure of solid ammonia from 176·92°K. to the m.p., 195·36°K., by the equation

$$\log p_{cm} = -(1630{\cdot}700/T) + 9{\cdot}00593$$

and of liquid ammonia from 199·26° to 241·59°K. by the equation

$$\log p_{cm} = -1612{\cdot}500/T - 0{\cdot}012311T + 0{\cdot}000012521T^2 + 10{\cdot}83997$$

giving 239·68°K. for the boiling point.

The vapour pressure of liquid ammonia from 30° to 132°C. is given in Table III.[58]

Table III.—Vapour Pressure of Liquid Ammonia

Temperature, °C.	Vapour pressure, atm.
30	11·515
50	20·074
70	32·717
90	50·526
110	74·83
130	107·6
132	111·5

Overstreet and Giauque measured the heat of fusion calorimetrically as 1351·6 ± 0·2 g.-cal. compared with 1376 g.-cal. as calculated from their vapour pressure measurements after correcting for gas imperfection by Berthelot's equation of state. Similarly for the heat of vaporization the calorimetric value is 5581 g.-cal./mole compared with 5614 g.-cal. calculated from the vapour pressure.[88]

Taylor and Jungers measured the vapour pressure of NH_3 and 99% ND_3 with the following results:

Temperature, °K.	V.p. NH_3, cm. Hg.	V.p. ND_3, cm. Hg.
202·3	77	63
213·0	184	154
226·1	364	313
232·1	511	445
238·6	714	628

The m.p. were 195·2°K. and 199·0°K., respectively, and the b.p. 239·75°K. and 242·3°K. The latent heat of vaporization of ND_3 was 193 g.-cal./mole higher than that of NH_3.[89]

Kirshenbaum and Urey found for the vapour pressures of solid NH_3 and solid ND_3 containing 98% of D:

$$\log (P_{NH_3}/P_{ND_3}) = 49{\cdot}69/T - 0{\cdot}1305$$

and for the vapour pressures of the liquid compounds:

$$\log (P_{NH_3}/P_{ND_3}) = 4625/T - 0{\cdot}14003$$

These equations give a difference in the heat of sublimation of 227 g.-cal. and in the heat of vaporization of 212 g.-cal. The triple-point temperatures are 195·68 and 198·79°K. and the triple point pressures 4·557 and 4·822 cm. for NH_3 and ND_3 respectively. The b.p. of ND_3 is 2·37° higher than that of NH_3.[90]

The vapour pressure differences between 70·6% $^{15}NH_3$ and ordinary NH_3 from 197·7 to 239·5°K. can be represented by the equation:

$$\log_{10} (P_1/P_2) = (0{\cdot}9593/T) - 0{\cdot}00325$$

where P_1 is the vapour pressure of ordinary NH_3 and P_2 is that of the 70·6% $^{15}NH_3$ material. At the triple points the vapour pressure of NH_3 is 4·561 cm. Hg. and that of 70·6% $^{15}NH_3$ is 4·574 cm. Hg, giving a m.p. difference of 0·083°K. or +0·118 ± 0·012°K. for pure $^{15}NH_3$

The b.p. of NH_3 is 239·68°K., while that of 70·6% $^{15}NH_3$ is 239·720°K., and thus that of pure $^{15}NH_3$ is 239·735°K.

The heat of vaporization of 70·6% $^{15}NH_3$ is 4·39 g.-cal. higher than that of NH_3 whence that of pure $^{15}NH_3$ is 6·25 g.-cal. higher.[91]

The fugacity coefficient p^*/p of saturated ammonia vapour is given by the equation:

$$\log p/p^* = p^{0{\cdot}5889}/43{\cdot}47$$

where p is in m. Hg., over the range 243° to 373°K.[92]

The m.p. of solid ammonia is related to the pressure over the range 300 to 3000 atm. by the empirical equation[93]:

$$p = 16{,}290 + 310{\cdot}22T + 1{\cdot}33044T^2$$

VISCOSITY

The viscosity of gaseous ammonia has been determined from 20° to 440°C. by damping of torsional oscillations of a quartz disc,[94] and from 20° to 716°C. by a capillary method.[95] Table IV shows the range of values.

Table IV.—Viscosity of Gaseous Ammonia

Temp., °C.	20	65·6	132·1	244·0	496	640	716
$\eta(\times 10^7)$, poise	982·1	1168·7	1437·0	1853·3	2660	3190	3648

The pressure range was extended to 26 atm. to include the region of liquefaction from −20° to 80° using a falling cylinder technique.[96] A later torsional-oscillations method, claiming a relative accuracy of 0·1%, gave 102·28 and 67·52 micropoises at 24·27° and −71·45° respectively.[97] More recently values at pressures up to 72.6 atm. and temperatures up to 300° (232 micropoises) have been obtained using a rolling-ball method.[98, 99]

The value of the Sutherland constant, C, in the equation,

$$\eta = \frac{KT^{3/2}}{C+T}$$

does not agree with that calculated from the Falkenhagen equation,

$$C = \frac{16\alpha\mu^2}{k\sigma^6}$$

where α = polarizability, μ = dipole moment, k = Boltzmann's constant and σ = molecular diameter. This was discussed in a study of the influence of the dipole moment on the magnitude of the Sutherland constant.[94] A mean value of C for the range 20–100° has been given as 505, and the temperature coefficient of the viscosity, n, in the equation,

$$n = [\log(\eta_2/\eta_1)]/[\log(T_2/T_1)]$$

over the same range, as 1·10.[100] The viscosity/temperature curve obeys Sutherland's equation at high temperatures, where the curve is concave, but departs from it below room temperature where it becomes convex to the temperature axis. An empirical equation is suggested for the range 23° to −80°.[97]

The viscosity of liquid ammonia has also been determined by a capillary method[101] and by using a rolling-ball viscometer.[102] Some results obtained by the latter method are given in Table V.

Table V.—Viscosity of Liquid Ammonia

Temperature, °F.	40°	100°	160°	220°
Pressure lb./sq. in.	Viscosity, micropoises			
Bubble point	1880	1306	748	(240)
1000	1911	1338	772	(243)
2000	1940	1367	822	304
4000	3004	1427	910	390
6000	—	—	1000	468

(The values in parentheses involve extra uncertainty)

The usual expression for the relationship between fluidity ($\phi = 1/\eta$) and the absolute temperature (T) does not hold for liquid ammonia. The equation:

$$\phi T^{3/2} = ae^{b/T}$$

where a and b are constants, gave better agreement with experimental values.[103]

The relation of viscosities in the liquid and saturated vapour state at a given temperature can be represented by the same curve for ammonia, carbon dioxide, sulphur dioxide and methyl chloride. Thus the viscosity in one state can be determined approximately from the curve if the value for the other state is known.[104] The viscosities of mixtures of ammonia with hydrogen, nitrogen, oxygen, ethylene, methane and air have been measured.[105, 106]

EFFUSION AND DIFFUSION

The rate of effusion of ammonia from capillaries has been shown to be a simple function of their diameter and the pressure differential.[107] Effusion in regions of critical flow velocities has been studied.[108, 109]

The diffusion coefficient, referred to air, determined by Lohschmidt's method was found to be 0·225 and 0·198 cm.^{2}/sec. at 20° and 0° respectively.[110, 111] A method of calculating the diffusion coefficient from viscosity data has also been described.[112–114]

The calculated self-diffusion coefficient for ammonia at 0°C. and 760 mm. is 0·193 cm.^{2}/sec. For the diffusion coefficient of ammonia in hydrogen the calculated value is 0·629 cm.^{2}/sec. compared with an observed value of 0·604 cm.^{2}/sec., and for ammonia in carbon dioxide the calculated and observed values are 0·151 and 0·155 cm.^{2}/sec. respectively.

In a two-bulb isotopic thermal diffusion experiment using about 15% of ^{15}N it was shown that the thermal diffusion constant α changes from positive to negative at about room temperature.[115] The thermal separation ratio at 450°K., calculated from the viscosity temperature coefficient, is given as $-0{\cdot}10$.[116]

With mixtures of ammonia and neon the thermal diffusion factor changes sign with composition. With 0–75% of neon the neon molecules diffuse up the temperature gradient; with more than 75% of neon they concentrate at the low temperature end.[117, 118] This is due to the opposing effects of differences in diameter and mass, neon having the smaller diameter but the larger mass. With equimolar mixtures of ammonia and nitrogen the thermal diffusion factor decreases with increasing pressure, changing sign at 1·8 atm., as a result of the non-ideal behaviour of gaseous ammonia.[119] Mixtures of ammonia and oxygen have also been studied.[120]

THERMAL CONDUCTIVITY

The thermal conductivity (K) of gaseous ammonia was measured as $551{\cdot}9 \times 10^{-7}$ g.-cal. cm.$^{-1}$ sec.$^{-1}$ degree C.$^{-1}$ at a mean temperature of 11·93°C. in the pressure range 1·25–7·58 cm. Hg. Linear extrapolation of the graph of values down to 4°C. gave 522×10^{-7} at 0°C. The temperature coefficient was 0·0048 degree C.$^{-1}$.[121] These values are in fair agreement with those obtained by a similar hot-wire method from 0·1–0·5 atm.[122] shown in Table VI.

Table VI.—Thermal Conductivity of Gaseous Ammonia

Temperature, °K.	$K \times 10^7$
273	516
300	587
350	727
400	868
450	1031
500	1192
550	1354
600	1490

Values obtained at higher pressures by a concentric cylinders method[123] are shown in Table VII.

Table VII.—Effect of Pressure on the Thermal Conductivity of Gaseous Ammonia

Temperature, °C.				
50°	P(atm.)	0	5·3	8·5
	Conductivity	646	674	696×10^{-5}
150°	P(atm.)	0	4·9	9·0
	Conductivity	968	985	1013×10^{-4}
250°	P(atm.)	0	5·4	9·0
	Conductivity	1371	1384	1406×10^{-4}

Above about 65°C. these latter values are significantly greater than those obtained by the hot-wire method,[122] and, if the thermal conductivity/temperature relationship is linear, below this temperature they fall below other 'hot-wire' values.[121, 122, 124] The thermal conductivity increases with increase of an applied electrostatic field.[125]

The variation of thermal conductivity with temperature has been presented as a nomograph[126] and is related to viscosity and diffusion data by an equation which is claimed to give good agreement with experimental data. Thus a value of 585×10^{-7} was calculated for K at 0°C.[127] The pressure coefficient over the range 1–9 atm. is represented as a simple function of the temperature and pressure,[123] and up to 60 kg./sq. in. and 150°C. as a function of the specific heat and specific volume.[128]

The thermal conductivity of ammonia has been used as a basis for the determination of ammonia in automatic gas analysis.[129]

The thermal conductivity of solid ammonia at $-103{\cdot}9$°C. is $0{\cdot}00239 \pm 0{\cdot}00001$ g.-cal. cm.$^{-1}$ sec.$^{-1}$.[130]

Owing to its use in refrigeration, liquid ammonia has been subjected to several calculations of its heat transfer coefficient.[131–133] Measurements of the transmission of heat both in condensation[134] and in boiling[135, 136] have been made and the extent of supercooling of liquid drops has been studied.[137]

The thermal conductivities of mixtures of gaseous ammonia with ethylene, air and carbon monoxide have been measured.[138, 139]

SURFACE TENSION

The surface tension of liquid ammonia has been measured in the presence of nitrogen, hydrogen, methane and carbon dioxide in the pressure range 1–800 atm. at 0–75°C.[140]

VELOCITY OF SOUND IN AMMONIA

Kaye and Sherratt[141] measured the velocity of sound in ammonia at 18° and 100° in glass, copper and carbon tubes of different diameters using the resonating tube method at frequencies from 500 to 7908 c./sec. The effects of tube diameter and frequency are given by the Helmholtz-Kirchhoff formula:

$$V = V_0\left\{1 - \frac{C}{2r(\pi n)^{1/2}}\right\}$$

where V_0 = the velocity in free space of sound of frequency n,
V = the velocity in a tube of radius r.

V_0 showed no variation with frequency or tube material and was 428·2 m./sec. at 18°C. and 481·9 m./sec. at 100°C. The Kirchhoff constant C varied with tube material and was 10% less than the theoretical value for the smooth copper and glass tubes and 30% more for the rough carbon tube. Variation of Kirchhoff's constant with temperature in the range 20–900°C. has been measured.[142]

Some measurements[143] of the velocity of sound as a function of pressure at ultrasonic frequency (514·5 kc./sec.) are given in Table VIII; these fit the equation:

$$W = W_0\left(1+\frac{S}{RT}\cdot p\right)$$

where W = the velocity of pressure p, and $W_0 = (C_p/C_v)_{p=0} \times \frac{RT}{M}$ to give values of $(C_p/C_v)_{p=0}$

Table VIII.—Velocity of Sound and Values of C_p/C_v for Gaseous Ammonia

Temp., °K.	P, atm.	W, m./sec.	W_0, m./sec.	$(C_p/C_v)_{p=0}$
242·1	0·993	398·0		
	0·601	400·3		
	0·263	401·7	403·3	1·368
254·1	0·942	403·3		
	0·647	404·5		
	0·263	406·5	407·5	1·336
264·1	0·921	407·7		1·307
273·1	0·947	414·7		1·305
301·5	0·967	432·2		1·277

The observed values of the constant S are in satisfactory agreement with values calculated from the second virial coefficient. The velocity is 430·4 m./sec. at 20°C., 2·993 kc./sec., and a pressure of 52·9 cm. Hg and 435·9 m./sec. at 3·10 cm. Hg.[144] The relaxation time is $8{\cdot}1 \times 10^{-10}$ sec.; other measurements are $1{\cdot}9 \times 10^{-7}$ sec.[145] and $1{\cdot}2 \times 10^{-7}$ sec.[146] From measurements at 0·6–3·0 atm. and 200–600 kc./sec. the relaxation times for the two normal vibrations were calculated as $0{\cdot}18 \times 10^{-6}$ sec. and $1{\cdot}45 \times 10^{-6}$ sec. at 30°C., and $0{\cdot}08 \times 10^{-6}$ sec. and $0{\cdot}32 \times 10^{-6}$ sec. at 100°C.[147] Measurements at 300 to 1000 kc./sec. indicated an anomalous dispersion due to inversion of the ammonia molecule.[148]

The temperature dependence of the velocity of sound in some liquefied gases, including ammonia, was found to be inversely proportional to the boiling point.[149]

SPECIFIC HEAT

The calorimetric values of the specific heat at constant pressure (C_p) from −30° to 150°C. determined by Osborne and co-workers have not been superseded (Mellor, VIII, 179). Overstreet and Giauque[88] have extended the measurements to the liquid and solid states and a selection of their values is given in Table IX.

Table IX.—Heat Capacity of Solid and Liquid Ammonia, C_p = g.-cal./degree mole

Temperature, °K.	20	40	60	80	100	120
C_p	0·368	1·841	3·474	4·954	6·246	7·497
Temperature, °K.	140	160	180	200	220	240
C_p	8·699	9·846	11·03	17·58	17·90	18·12

The authors showed that generally their values, which agree well with spectroscopic values, were between 0·5 and 14% less than earlier figures. For temperatures below 20°K. the experimental data obeyed the equation:

$$C_p = 4{\cdot}73(10^{-5})T^3$$

where T is the absolute temperature.[150]

Many calculations of specific heats have been made from spectroscopic data. Earlier calculations used a rigid rotator-harmonic oscillator model, and values were obtained from 273° to 2800°K.[151–153] Stretching of the molecules by centrifugal force and by interaction of rotation and vibration were taken into account in obtaining a good fit to the data of Osborne and co-workers from 0° to 150°C.[154] Other studies on the effect of rotational distortion have been made.[155, 156] The effect of the double potential minimum due to the resonance of the nitrogen atom through the plane of the three hydrogen atoms has been discussed and applied. The range of validity for the classical expression for the rotational heat capacity has also been given.[157]

More recently, however, Godnev has shown that the double minimum effect is negligible. He has calculated the internal C_p and total C_p values for two spin modifications and their equilibrium mixture from 5° to 100°K.[158] Other calculations of the specific heat at high temperatures[159] and high pressures (20–1000 atm.) have been made[160] and discussed.[161] One of the most recent calculations of the specific heat from −40° to 1200°C. includes the effects of the double minimum and centrifugal distortion, but regards as negligible contributions from rotation–vibration interaction and Kassel's rotational partition function. Agreement is obtained with the experimental values of Osborne and co-workers within the limits of their accuracy. Since systematic procedures were used in the calculations the authors believe the values to be as accurate beyond the experimental range.[162] A selection of these values is given in Table X.

Table X.—Heat Capacity of Ammonia from Spectroscopic Data

(Heat Capacity in g.-cal./degree mole)

Temperature, °K. C_p	233·16 8·180	253·16 8·268	273·16 8·371	295·16 8·514	400 9·241	600 10·808
Temperature, °K. C_p	800 12·225	1000 13·467	1200 14·530	1500 15·791		

A formula for the heat capacity of partially dissociated ammonia gas has been derived.[163]

Equations for the variation of heat capacity with temperature have been given for temperatures below 20°K.[150] and above that temperature.[155, 162] For the expression:

$$C_p^\circ = a + bT + cT^2 + dT^3$$

where T is the absolute temperature, $a = 6{\cdot}5846$, $b \times 10^3 = 6{\cdot}1251$, $c \times 10^6 = 2{\cdot}3663$, $d \times 10^9 = -1.5981$; the average deviation is 0·36% and the maximum 0·91% for the range 233° to 1500°K.[162, 164] Simple approximation equations are given by Beattie for the specific heat both at constant pressure and at constant volume[165]; the constant pressure equation has been modified to give more accurate values from 0 to 20 atm. and 0° to 150°C.[166]

Selected values of the specific heat at constant pressure have been tabulated for 273° to 2800°K.,[51] 300° to 600°K.,[167] 0° to 1200°C.,[164] 0° to 600°C.[168] and below 60°F.[169] Literature surveys and a number of compilations for more technical purposes[171–177] have been made.[167, 170]

The change in internal energy with pressure has been experimentally determined and the results agree with values calculated from the Beattie–Bridgman equation of state.[178] Values of the specific heat at constant volume have been reviewed; at 273·1°K., $C_v = 6{\cdot}38$ g.-cal./degree mole.[179]

ENTHALPY

Table IX gives values calculated by Harrison and Kobe[162, 164] for the enthalpy of ammonia in the ideal gas state relative to the enthalpy at 0°C., obtained by graphical integration of their specific heat values and values of the enthalpy function calculated from spectroscopic data.

Table XI.—Enthalpy of Gaseous Ammonia

Temperature, °K.	$H^\circ - H^\circ_{273}$	$\dfrac{H^\circ - H_0^\circ}{T}$
	g.-cal./mole	g.-cal./degree mole
233·16	−330·84	7·9951
253·16	−166·41	8·0130
273·16	0	8·0355
298·16	210·70	8·0685
400	1,113·6	8·2715
600	3,120·1	8·8585
800	5,426·3	9·5266
1,000	7,998·0	10·193
1,200	10,801	10·830
1,500	15,359	11·703

The National Bureau of Standards[169] gives values for the enthalpy of ammonia at various pressures below 60°F. and Grahl[180] gives similar data for temperatures from −100° to 700°F. and pressures from 0 to 16,000 lb./sq. in.

ENTROPY

Early values of the entropy of the ideal gas at 298·1 °K. varied from 44·1 from spectroscopic data[181] to 47·2 g.-cal./degree mole from low temperature calorimetric data[182, 183] Overstreet and Giauque obtained more accurate low temperature calorimetric data and were able to secure good agreement between a revised spectroscopic value of 45·91 and the experimental value of 45·94±0·10, which had been corrected to the ideal state using Berthelot's equation of state and the expression:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

The corresponding values at the b.p. of liquid ammonia, 239·68°K., were 44·10 and 44·13. These values omit, as is customary, the nuclear spin entropy $R \ln 24 = 6{\cdot}31$ g.-cal./degree mole.[88] This is the entropy value of crystalline ammonia at 0°K. with the two symmetry varieties present in equal amounts.[184] The entropy correction for the effect of centrifugal distortion is given as $S = S' + 2pRT$ where S' is the 'rigid rotator' entropy value and $p = 1{\cdot}45 \times 10^{-5}$ for ammonia.[156] The magnitude of the error caused by the double potential minimum effect in the classical expression for the rotational entropy is less than 0·05 g.-cal/degree mole provided that

$$T > T_0 = 1{\cdot}5 \times 10^{-38} n/I$$

where I = moment of inertia in g. cm.^{2}, n = symmetry number about the same axis and n/I has the maximum value. The error falls rapidly as $1/T^2$ with increase in temperature above T_0.[157] However, Godnev has shown that even at low temperatures the effect is insignificant and has tabulated the entropy from 5° to 100°K. for the two spin modifications and the equilibrium mixture.[158] Table XII gives a range of values and shows the degree of agreement now reached.

Table XII.—Entropy of Ammonia from Spectroscopic Data, S°
(g.-cal./degree mole)

Temperature, °K.	Stephenson & McMahon[185]	Harrison & Kobe[162, 164]
233·16	—	43·984
253·16	—	44·660
273·16	—	45·293
298·16	46·034	46·026
400	48·628	48·633
600	52·602	52·680
800	55·915	55·988
1000	58·757	58·852
1200	61·296	61·404
1400	63·598	63·713
1600	65·704	—
1800	67·641	—
2000	69·434	—

Similar values have been given for the range 291·16° to 1000°K.[153] and values have been calculated for the pressure range 20 to 1000 atm. at 150° to 300°C.[160] Data obtained by statistical and spectroscopic methods have been compared with values obtained by means of the Nernst heat theorem,[186] and calculations of values at high temperatures from molecular and atomic spectra have been discussed in detail.[159]

After reviewing the existing equilibrium data and correcting for gas imperfection Gillespie and Beattie calculated the entropy of formation of ammonia at 0°C. and 1 atm. as −23·054 g.-cal./degree mole.[187] From the entropies of crystalline ammonia, nitrogen and hydrogen at 0°K. Sterne obtained

$$\Delta S_0^\circ = -(9/8)R \ln 3 \text{ g.-cal./degree mole}^{184}$$

whilst from band spectra Stephenson and McMahon calculated

$$\Delta S^\circ_{298\cdot 1} = -23\cdot 71 \text{ g.-cal./degree mole}^{185}$$

FREE ENERGY FUNCTION

Values calculated from spectroscopic data are given in Table XIII.

Table XIII.—Free Energy Function of Ammonia

$$\frac{(F^\circ - H_0^\circ)}{T} \text{ g.-cal./degree mole}$$

Temperature, °K.	Stevenson & McMahon[185]	Thomson[153]	Harrison & Kobe[162, 164]
273·16	—	—	37·26
298·16	37·989	37·964	37·96
400	40·380	40·362	40·36
600	43·826	43·818	43·82
800	46·450	46·428	46·46
1000	48·634	48·601	48·66
1200	50·535	—	50·57
1500	53·033	—	53·09
2000	56·559		

HEAT OF FORMATION AND FREE ENERGY OF FORMATION

Kelley has given the heat of formation at 298·1°K. from the elements in their standard states as −11,040 g.-cal./mole[152] and this value has been generally adopted.[162, 164, 188] He gave the free energy of formation as $-3{,}980$ g.-cal./mole. The variations of these quantities with absolute temperature are given by the equations

$$\Delta H^{\circ} = 9560 - 606T + 2{\cdot}19 \times 10^{-3}\,T^{2} + 0{\cdot}398 \times 10^{3}\,T^{-1}$$

and

$$\Delta F^{\circ} = 9560 + 13{\cdot}96T \log_{10} T - 2{\cdot}19 \times 10^{-3}\,T^{2} + 0{\cdot}199 \times 10^{5}\,T^{-1} - 15{\cdot}39T$$

From the thermal value $\Delta H^{0}_{298\cdot 1} = -11{,}040$ g.-cal./mole, and their spectroscopic values for the free energy function and entropy, Stephenson and McMahon[185] obtained $\Delta H_{0}^{\circ} = -9364$ g.cal./mole but preferred $\Delta H_{0}^{\circ} = -9254$ obtained from equilibrium data which were considered more accurate than the thermal data for $\Delta H^{\circ}_{298\cdot 1}$. Harrison and Kobe have adopted $\Delta H_{0}^{\circ} = -9205$ g.-cal./mole and $\Delta F^{\circ}_{298} = -3860$ g.-cal./mole.

Values of the free energy of formation at various temperatures given by Harrison and Kobe and values calculated from Kelley's equation[188] are given in Table XIV.

Table XIV.—Free Energy of Formation of Ammonia, ΔF° g.-cal./mole

Temperature, °K.	Kelley	Harrison & Kobe
298·1	−3,980	−3,860
400	−1,480	−1,330
600	3,730	3,950
800	9,170	9,470
1000	14,760	15,110
1200	20,380	20,790
1500	—	29,350

The following alternative expression for ΔF° has been derived[189]:

$$\Delta F^{\circ} = -9172 + 17{\cdot}387 \log T - 0{\cdot}003992T^{2} + 0{\cdot}334 \times 10^{-6}\,T^{3} - 24{\cdot}44T$$

and calculations have been made over the range 150–300°C. and 20–1000 atm.[160]

Heats of formation at 0–1200°K. and 1–3000 atm.[190] have also been calculated; Gillespie and Beattie[191] give the values quoted in Table XV.

Table XV.—Heat of Formation of Ammonia, kcal./mole

Temperature, °C.	0	300	500	600	700
Pressure, atm.					
1	10·63	11·99	12·66	12·89	13·04
100	—	12·43	12·92	—	13·23
300	—	13·32	13·45	—	13·61
600	—	14·66	14·24	—	14·19
1000	—	16·44	15·29	—	14·95

By measuring the thermal losses from a heated molybdenum wire, functioning as a catalyst, the mean value of the heat of dissociation of ammonia from 954° to 1164°K. was obtained as 12,067 g.-cal./mole. Thermodynamic data gave 13,375 g.-cal./mole. The discrepancy is attributed to chemical reaction with the molybdenum.[192]

ELECTRICAL CONDUCTIVITY

The specific conductance of solid ammonia, determined at frequencies of 60 and 0·3 kc./sec., is given in Table XVI[5]:

Table XVI.—Specific Conductance of Solid Ammonia, $K \times 10^9$ (ohm^{-1} cm.$^{-1}$)

Temperature, °K.	60 kc./sec.	0·3 kc./sec.
172·9	0·9	0·2
177·3	2·6	2·1
188·6	7·0	3·3
194·1	8·4	3·5

Measurement of the specific conductance of liquid ammonia gave $1{\cdot}2 \times 10^{-7}$ mhos at 201·7°K. and $1{\cdot}97 \times 10^{-7}$ at 234·3°K.[193, 194] From the e.m.f. of cells of the type: NH_4 amalgam/NH_4I(concn. C_1)/KI(saturated soln.)/NH_4I(concn. C_2)/NH_4 amalgam the ionic product for $(NH_4^+) \times (NH_2^-)$ of liquid ammonia is calculated to be $10^{-29 \pm 1}$.[194, 195]

DIELECTRIC CONSTANT AND DIPOLE MOMENT

A selection of the values of the dielectric constant of solid ammonia obtained by Smyth and Hitchcock[5] is given in Table XVII.

Table XVII.—Dielectric Constant of Solid Ammonia

Temperature, °K.	60 kc./sec.	5 kc./sec.	0·3 kc./sec.
87·0	3·37	3·36	3·36
110·5	3·40	3·41	3·39
136·9	3·42	3·41	3·41
172·9	3·46	3·48	3·63
188·6	3·67	3·90	4·62
194·1	3·84	4·03	4·83

The dielectric constant of liquid ammonia is 18·94 at 5°C., 17·82 at 15°C., 16·90 at 25°C. and 16·26 at 35°C.[196] Smyth and Hitchcock[5] obtained 25 at −77·7°C. The theoretical relationship between the dielectric constant and dipole moment of liquid ammonia has been discussed.[197, 198] The molar polarization at 25°C. is 23·8 c.c.[199]

The dielectric constant of gaseous ammonia can be used to calculate the molar polarization P using the Mosotti–Clausius equation:

$$P = \frac{\epsilon - 1}{\epsilon - 2} \times \frac{M}{D}$$

where ϵ = dielectric constant, M = mol. wt. and D = density. As this equation is valid only for perfect gases, LeFèvre and Russell[200] extrapolated their measurements to zero pressure to obtain the values given in Table XVIII:

Table XVIII.—Molar Polarization of Ammonia

Temperature, °K.	P
293·8	50·22
318·0	47·20
346·8	44·00
375·4	40·65
419·4	36·93

These values were fitted to the Debye equation, $P = P_D + 4/3\pi N\left(\frac{\mu^2}{3kT}\right)$, to obtain the distortion polarization $P_D = 5{\cdot}90$ and the dipole moment $\mu = 1{\cdot}45$ D.

Table XIX gives values of the polarizations of ammonia and deutero-ammonia reported by de Bruyne and Smyth.[201]

Table XIX.—Molar Polarization of Ammonia and Deutero-Ammonia

NH_3		ND_3	
Temperature, °K.	*P*	Temperature, °K.	*P*
273·9	53·79	274·1	54·94
309·2	48·30	304·3	49·85
334·9	45·29	333·8	45·85
363·6	41·93	363·8	42·46
394·0	39·05	394·2	39·38
423·1	36·67	425·0	37·04

Application of the Debye equation gives, for NH_3, $P_D=5{\cdot}3$ and $\mu=1{\cdot}466$ D., for ND_3, $P_D=4{\cdot}4$ and $\mu=1{\cdot}496$ D. The difference between the dipole moments of NH_3 and ND_3 is due to the effect of the zero point energy on the anharmonic vibration of the nitrogen atom at right angles to the plane of the hydrogen atoms.

Values of the dielectric constant and molar polarization of ammonia are given for various temperatures at 1 atm. in Table XX, and for various pressures at 50°C. in Table XXI.[202]

Table XX.—Dielectric Constant of NH_3 at 1 atm.

Temp., °C.	$(\epsilon-1)10^6$	*P*, cm.^{3}
5·81	5803	51·75
38·72	5272	47·02
58·63	4994	44·54
80·33	4728	42·17
129·54	4209	37·56

Table XXI.—Dielectric Constant of NH_3 at 50°C.

Pressure, mm.	$(\epsilon-1)\times10^6$	*P* cm.^{3}
760	5,234	45·73
2,947	20,893	45·77
6,721	50,080	45·84
11,472	92,124	45·93

The dipole moment calculated from these figures is 1·437 D. Other measurements of the dipole moment of ammonia have given 1·44 D.,[203] 1·48 D.[204] and 1·437 D.[205] The dipole moment of ammonia is 1·38 D. in benzene solution and 1·43 D. in *n*-heptane solution.[206]

The dielectric constant of ammonia at 26°C., 730 mm. Hg pressure and 9400 Mc./sec. is $6{\cdot}8\times10^{-3}$.[207] The dielectric loss at 9280 Mc./sec. increases from $0{\cdot}01\times10^{-4}$ at 20 mm. Hg to $1{\cdot}0\times10^{-4}$ at 200 mm.[208] Other studies of the dielectric properties of ammonia at micro-wave frequencies have been made.[209–215]

The theory of dielectric polarization in polar substances was extended[216] to include the effects of fluctuations in the dipole moments of the individual molecules and of optical anisotropy; the contribution of these effects to the polarization of gaseous ammonia was calculated. Other authors have also given theoretical treatments of the polarization of ammonia.[217–220]

The deviation of a molecular beam of ammonia by an electric field has been studied by Scheffers[221, 222] The dipole moment of ammonia calculated from the results is only one-third of that obtained from dielectric constant measurements: this has been attributed to the effect of inversion of the ammonia molecule, an explanation which has been both opposed[223] and supported.[224]

REFRACTIVE INDEX AND KERR EFFECT

The refractive index, n, and molar refraction, R, of NH_3 and ND_3 are given in Table XXII.[225, 226]

Table XXII.—Refractive Index and Molar Refraction of Ammonia and Deutero-ammonia

	$(\eta-1)\times10^6$		R	
Wavelength, A.	NH_3	ND_3	NH_3	ND_3
6562·9	373·5	369·4	5·581	5·520
5893·0	375·8	372·6	5·615	5·568
5460·8	377·6	374·1	5·642	5·590
4916·0	381·3	378·2	5·698	5·651
4358·3	386·4	383·3	5·774	5·727

Values of the refractive index and dispersion for NH_3 were obtained by Craven[227] using a comparative method. Measurements of the Kerr effect were made at 6500 A. − 5750 A., pressures from 13 to 30 atm. and temperatures from 20° to 65° C. The value of the Kerr constant, reduced to N.T.P. and 6500 A., is $(62{\cdot}3\pm1{\cdot}8)\times10^{-12}$.[228] The Kerr effect has been discussed also by Stuart.[229]

FARADAY EFFECT

Verdet constants have been determined for liquid ammonia from −77°C. to −34°C. The molar rotation of the liquid is $13{\cdot}6\times10^{-5}$ radians and independent of temperature, whereas that of ammonia gas is $5{\cdot}51\times10^{-5}$ radians. The dispersion of the gas is the same as that of the liquid.[230, 231]

Measurements have been made of the Faraday effect and of magnetic birefringence at 23,870·1 Mc./sec.,[232] but no measurable effect was found at a wavelength of 3·3338 cm.[233]

The diamagnetic molecular susceptibility of ammonia in strong aqueous solution is $-17{\cdot}1\times10^{-6}$ c.g.s. units[234] compared with -19×10^{-6} in the gaseous state.

IONIZATION POTENTIAL

From photo-ionization measurements the ionization potential has been found to be $10{\cdot}13\pm0{\cdot}02$ ev.,[235] 10·25 ev.[236] and 10·07 ev.[237] The photoionization cross-section of NH_3 increased from $2{\cdot}0\times10^{-18}$ cm.^{2} at 1216 A. to 9×10^{-18} cm.^{2} at 1060 A.[236] At 824 A. the cross-section rises steeply from 10×10^{-18} to 30×10^{-18} cm.^{2} [237] possibly owing to the additional dissociation:

$$NH_3 \rightarrow NH_2^+ + H + e^-$$

McDowall,[238] however, considers that the ionization at 10·07 ev. consists in the removal of an electron from the (Za_1) orbital with the formation of NH_3^+ in its ground $^2A_1$ state, and the second ionization at 15·31 ev. concerns the removal of an electron from the degenerate [πe] bonding orbital to give a NH_3^+ ion in its ^2E first electronically excited state.

From electron impact measurements the ionization potential has been found to be

11·2 ± 1·5 ev.,[239] 10·5 ± 0·1 ev.,[240] 10·8 ev.,[241] 10·1 ev.[242] Neuert[243] obtained 11·30 ± 0·02 ev. for NH_3, 11·47 ± 0·02 ev. for ND_2H and 11·52 ± 0·03 ev. for ND_3.

The ions formed from NH_3 include NH_4^+, NH_3^+, NH_2^+, NH^+, N^+, H^+, NH_3^{++}, NH_2^-, NH^- and H^-.[239, 240, 244–247] The formation of a negative ion by electron attachment has been studied by a number of authors.[248–253]

The sparking voltage with ball electrodes is 36 kv. with a 1-cm. gap and 57 kv. with a 2-cm. gap.[254] When ammonia gas is flowing through a 10-cm. gap between a tubular and a disc electrode the sparking voltage is 55 kv.[255]

The scattering cross-section of ammonia for protons decreases from 73·5 $cm.^2/cm.^3$ at 1 mm. and 0°C. at 13 volts to 53·5 at 30 volts and about 38 at 90–240 volts. The proton affinity of ammonia calculated from these results is 9·4 ev.[256]

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PHYSICAL PROPERTIES OF MIXTURES OF GASES AND AMMONIA

Solubility

The solubility of hydrogen in liquid ammonia has been studied at pressures up to 1000 atm.[1] It rises with temperature and, in general, follows Henry's law,[2] the solubility in c.c. of hydrogen/100 c.c. of liquid NH_3, at 25°, being 97·3 at 15 atm., 610·6 at 100 atm. and 1575 at 250 atm. Nomographs for the solubility of both hydrogen and nitrogen in liquid ammonia are given.[3] The solubility of helium[2] also increases with increase in temperature and increase of pressure, being 11·56 at

5·2 atm. and 75·22 at 38·3 atm. The solubility of nitrogen within the range 25–1000 atm. at 25° was found to be 2·22 c.c. per g. of ammonia at 25 atm., rising to 54·83 at 1000 atm.[4]

The diffusion coefficient of hydrogen in liquid ammonia, studied[32] at 25° and 30° over the range 35–100 atm., has been found to be independent of pressure.

Experiments on the mutual solubility of various gases and ammonia have been carried out largely by Tsiklis. The systems NH_3–N_2, NH_3–CH_4, NH_3–N_2–CH_4 and NH_3–N_2–H_2 behave similarly, showing limited mutual solubility up to 148° and 9500 kg./cm.^{2} [5] The liquid–gas and gas–gas NH_3–N_2 equilibria curves have been extended above 148° and 9000 kg./cm.,[2, 7] the critical curve being extended up to 175° and 16,700 kg./cm.^{2} Curves have been given[6] for the pressures required for separation of liquid layers at ammonia concentrations from 0–100%, at various temperatures and with varying amounts of methane for the system NH_3–N_2–CH_4. From measurements at 120–200° in the pressure range 100–8600 kg./cm.^{2} limited mutual solubility is shown to exist for the system NH_3–He.[8] The critical pressure increases with the temperature very slowly. Results obtained by Tsiklis[9] on the mutual solubility of nitrogen, methane and ammonia disagree with the equation of Krichevsky and Hasanova.[10] Cupples[11] defines the solubility effect in the gaseous phase as a change in the activity of one component due to the presence of other components. In the system $NH_3(l)$–$NH_3(g)$, $H_2(g)$, $N_2(g)$, this effect is absent.

The solubility of liquid ammonia in compressed nitrogen at 75° and 80° at pressures up to 4000 atm. has been determined. The solubility curve has minima at about 500 atm. and 75° and 600 atm. and 80° [12]; the system also has a region of limited miscibility.

The volumes of ammonia–hydrogen mixtures in the liquid phase from 100 to 800 atm. at 100° have been measured and the partial molal volumes calculated.[13] The partial molal volume of ammonia decreases as the concentration of hydrogen increases. Volume and phase relations were studied for the systems NH_3–N_2 and NH_3–H_2 [14] and both obey the equations for dilute non-electrolytes. The NH_3–N_2 system has also been studied by Krichevsky and Bolshakov[15] who found that the critical curve possesses a temperature minimum between 85° and 90°. The gas–gas equilibrium was studied in the binary system NH_3–N_2 from 90–148° at pressures up to 10,000 kg./cm.^{2}, in the NH_3–CH_4 system from 45–100° at pressures up to 10,000 kg./cm.^{2}, and the ternary system NH_3–N_2–H_2 at 100° at pressures up to 5500 kg./cm.^{2} [16] An apparatus for studying gas–liquid phase equilibria in the system NH_3–H_2–N_2 has been developed[17] and used to investigate P–T–x relations in the range 10–800 atm. and 0–120°.

Compressibility

The compressibilities of CH_4–NH_3 and NH_3–H_2–N_2 mixtures have been determined[18, 19] over a range of temperatures and pressures. Kazarnovsky has developed[20] the equation of state for binary gas mixtures:

$$p = p_1^0 N_1 + p_2^0 N_2 + \alpha N_1 N_2 (p_1^0 - p_2^0)$$

The components of the mixture are dipoles with rectilinear isometrics and the coefficient, α, is a temperature function. The dependence of α on temperature was shown by the binary systems NH_3–N_2 and NH_3–H_2. The equation gives good agreement for the compressibility over a wide range of temperatures and pressures.

The fugacity equation, derivable from Dalton's law, was used in examining high pressure liquid–vapour equilibria in the presence of non-condensing components.[21] Data for the system NH_3–H_2–N_2 are given.

The Ammonia Equilibrium

Gillespie and Beattie[22, 23] have made a study of the equilibria involved in the Haber ammonia synthesis. All the data on the synthesis reaction over the range

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325–953° and 10–1000 atm. are correlated with compressibility and heat-capacity data by means of an equation for the mass-action function Kp. The optimum initial and equilibrium ratios of hydrogen and nitrogen were calculated. This equation gives a more accurate representation of the experimental data than the equations derived by Keyes and by Newton and Dodge.[24] A theoretical proof of Newton and Dodge's rule[25] is given by Brodsky.[26]

Maron and Turnbull have derived an equation for the activity coefficients of gases from the Beattie–Bridgeman equation of state and have applied this to the N_2–H_2–NH_3 system in order to calculate the activity coefficients and the equilibrium constant for the synthesis of ammonia.[30] Fuchs has shown that, at a sufficiently high temperature, the equilibrium constant formula can be expressed in terms of the van der Waals constants. A plot of observed and calculated values shows good agreement.[31] Other thermodynamic properties of the N_2–H_2–NH_3 system have been studied. Compressibility isotherms have been plotted and entropy, enthalpy, internal energy and specific heats at constant pressure calculated as a function of temperature and pressure.[28] Kazarnovsky has calculated the heat of mixing N_2+3H_2 with NH_3 and found that the heat of the reaction:

$$N_2+3H_2 \rightarrow 2NH_3$$

is only slightly affected by pressure, if allowance is made for the heat of mixing.[27]

Longuet-Higgins has applied a statistical approach to multi-component systems including nitrogen, hydrogen and ammonia.[29]

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PHYSICAL PROPERTIES OF SOLUTIONS OF METALS IN LIQUID AMMONIA

Solubility

Values for the solubilities of the alkali metals in liquid ammonia are given in Table XXIII.

Table XXIII.—Solubility of Alkali Metals in Liquid Ammonia

Metal	Temperature °C.				
Lithium[1]	−63·5°	−33·2°	0°		
	10·698	10·866	11·319 g./100 g. of NH_3		
	3·81	3·75	3·60 moles NH_3/Li		
Sodium[2]	−105°	−70°	−50°	−33·8°	0°
	—	—	—	24·64 g./100 g. of NH_3	
	—	—	—	5·42 moles NH_3/Na	
Sodium[3]	4·98	5·20	5·39	5·48	5·87 moles NH_3/Na
Potassium[4]	−50·38°	−33·5°	0°		
	45·47	46·39	49·08 g./100 g. of NH_3		
	5·05	4·95	4·68 moles NH_3/K		
Caesium[5]	−50·0°				
	77·05 g./100 g. of NH_3				
	10·13 moles NH_3/Cs				

Density

Unusually large increases in volume occurring on dissolution of the alkali metals in liquid ammonia have directed attention to the determination of the densities of the solutions. Lithium ($d_{20} = 0{\cdot}53$ g./c.c.) gives at −33·2° a steadily declining density from 0·639 g./c.c., at a mole fraction of 0·0331 to 0·490 g./c.c. at 0·2105 (saturated). However, the difference in volume, ΔV, per mole of solute, between that of the solution and the sum of the volumes of the components shows a maximum of 46 c.c. which approaches, but is greater than, that shown by solutions of sodium and potassium.[6, 7] Density values for sodium ($d_{-33{\cdot}8} = 0{\cdot}9805$ g./c.c.) solutions at −33·8° increase steadily from 0·5781 g./c.c. at 5·45 moles NH_3/Na (saturated) to 0·6704 g./c.c. at 64·14 moles NH_3/Na. The corresponding values of ΔV are 41·01 c.c. and 39·51 c.c. with a maximum value of 43·37 c.c. at 11·25 moles NH_3/Na.[2] Kikuti[8] has given values from −28° to 30°.

Stosick and Hunt[9] were unable to reproduce the very large molar volume of sodium in liquid ammonia solutions found by Ogg,[10] but confirmed the values given by Kraus.[11] Potassium ($d_{20} = 0{\cdot}86$) solutions at −33·2° range in density from 0·6282 at 4·95 moles NH_3/K (saturated) to 0·6721 at 34·08 moles NH_3/K. The values of ΔV are, respectively, 27·28 c.c. and 24·73 c.c. with a maximum of 29·80 c.c. at about 10·5 moles NH_3/K.[2]

The density of saturated solutions of sodium and potassium increases by about 0·1% per degree fall in temperature.[6] At −50°, ΔV for caesium is 16·2 ml. per g.-atom of Cs at an NH_3/Cs ratio of 6·12, and 3·1 ml. at a ratio of 30·60. No separation into two liquid phases occurs down to −70° for caesium concentrations between

0·04 M. and 7 M. The density of solutions of caesium ($d_{-50}=1·927$) falls smoothly from 1·0140, $NH_3/Cs=6·12$, to 0·8041 g./ml., $NH_3/Cs=30·60$.[5]

Kraus and Lucasse have shown that a liquid–liquid phase separation occurs in sodium solution at an upper consolute temperature of −41·6° and a composition of 95·85% mole of ammonia. At −60° the phases contain 98·2% and 91·7% mole of ammonia.[12] Sodium iodide decreases the miscibility of the two phases.[13] Similarly potassium iodide solutions are miscible with dilute potassium solutions, but not with concentrated solutions.[14] Liquid–liquid phase separation probably occurs for potassium above the m.p. of ammonia. Phase diagrams for lithium, potassium, calcium, strontium and barium below this temperature have been constructed[15] and the melting points of the eutectics of lithium, sodium, potassium and calcium were found to be approximately −185°, −110°, −157° and −90° respectively.[16]

Vapour Pressure

Vapour pressures of saturated solutions of lithium in liquid ammonia are given by Johnson and Piskur[1]:

Temperature, °C.	V.p., mm. Hg	Moles NH_3/Li
0	34·0	3·60
−33·2	3·4	3·75
−63·5	1·1	3·81

Values for saturated solutions of potassium were found by Johnson and Meyer[4]:

Temperature, °C.	V.p., mm. Hg	Moles NH_3/K
0	750	4·68
−33·5	162	4·95
−50·38	63	5·05

The vapour pressure curve for caesium falls below the Raoult's Law curve.[5] Thus, at a mole ratio NH_3/Cs of 9·24, the vapour pressure is 245·7 mm. Hg at −50°C., giving an apparent gram atomic weight of 54·6. This is similar to the behaviour of solutions of lithium, sodium and potassium, each of which in dilute solution appears to give an atomic weight which is too small. The vapour pressures of calcium, strontium, barium, lithium and sodium solutions in liquid ammonia as functions of concentration and temperature have also been determined.[19]

Thermodynamic Properties

The activities of lithium, sodium and potassium are greatly reduced as the concentrations of the metals decrease. Thus the activity of potassium changes by a factor of 25,000 for a concentration change of 2·571 whilst for lithium the activity change is 3×10^9 for a fourfold change of concentration. For sodium the change is less than for potassium.[17]

By an amalgam-partition method the free energy of formation of the sodium ion in liquid ammonia, relative to potassium and rubidium, was found to vary from 3·22 to 3·30 and from 2·9 to 3·0 kcal./mole respectively.[18]

The atomic heat of solution of lithium in liquid ammonia at −33° is given[20] as $-9·65\pm0·2$ kcal. for the concentration range 150–600 moles NH_3/g. atom Li. This value is higher than those previously observed: −7·96 to −8·06 kcal.[21] and −7·96 to −8·42 kcal.[23] Values for sodium range from +1·36[21] to +1·45 kcal.[22] Potassium gives either a zero heat of solution[23] or a slightly endothermic value, −14 g.-cal.[21]

No heat effects were observed on dissolution of rubidium and caesium, but values found[23] for the alkaline earth metals were:

Ca	−9·76	to	−10·78 kcal.
Sr	−17·35	to	−19·38 kcal.
Ba	−11·02	to	−16·12 kcal.

However, a more recent determination[24] for calcium has given −19·7 kcal. at −33°. The high values are considered to be due, in part, to the heat of reaction forming an ammoniated metal ion.

Coulter and Maybury[26] have given the heat changes, ΔH°, for the reaction

$$M + NH_4^+ \rightarrow M^+ + NH_3(l) + \tfrac{1}{2}H_2$$

and, taking the electrode potentials found by Pleskov and Monoszon,[25, 89] they calculated, for the above reaction, the free energies, ΔF°, the partial molal ionic entropy at −33°, $S^\circ_{240^\circ K}$, relative to $\bar{S}^\circ_{NH_4^+} = 0$, and the entropies of solvation of the ions, ΔS.

	Li	Na	K	Rb	Cs
ΔH° (kcal./equiv.)	−50·6	−38·7	−39·7	−40·0	−41·6
ΔF° (kcal.)	−51·4	−42·4	−45·6	−44·4	−44·9
$\bar{S}^\circ_{240^\circ K}$ (g.-cal./deg.)	−26·8	−9·5	+2·6	−2·4	−3·0
ΔS (g.-cal./deg.)	−52	−38	−27	−34	−42

The very similar values for ΔH° indicate an identical reaction in each case, and consequently close similarity in the nature of the dilute solutions of the alkali metals in ammonia.[26] ΔH° for calcium for the heat of reaction $Ca + NH_4^+$ is −99·3 kcal.[24] For the reaction:

$$e_2^{=}(am) + 2NH_4^+(am) \rightarrow 2NH_3(l) + H_2(g)$$

where (am) indicates (in liquid ammonia), $\Delta H = -79{\cdot}7$ kcal. This result agrees with that obtained for the alkali metals,[20, 26] and signifies two-electron ionization of the calcium atom.[24] Thermochemical data of the alkali metals and the more common ions have been calculated by Jolly.[27] Coulter[28] has discussed the thermochemistry of alkali and alkaline earth metals and their salts in liquid ammonia in interpreting their behaviour in this solvent. The heat of ammoniation of the electron was calculated to be 11 ± 4 kcal. The standard molar entropy of ammoniated electrons has been calculated[29] from thermo-electronic data as 65 ± ~5 ev. at −33°, which is at variance with the value −25 ev. obtained by Latimer and Jolly.[30] Equations and tables are given by Jolly[31, 32] for the estimated heats, free energies and entropies for species in liquid ammonia.

Electrical Conductivity

The specific conductivities of saturated solutions of sodium and potassium at −33·5° were measured by Kraus and Lucasse[35] as $5{\cdot}047 \times 10^3$ and $4{\cdot}569 \times 10^3$ mhos respectively, of the same order of magnitude as that of metallic iron. More dilute solutions approach values associated with aqueous solutions of electrolytes. The experimental results for the alkali metals have been interpreted on the basis of the presence of free electrons.[37–39]

Density measurements[2, 11] have been used to calculate[36] the atomic conductivities of sodium and potassium solutions; the temperature coefficient of resistance of the former is always negative and its magnitude increases as the temperature decreases.[40] Deigen[41] has explained the dependence of electrical conductivity and the temperature coefficient of conductivity on the concentration of the metal using the concept of solutions as ionic dielectrics and the theory of polarons. A Wien effect of 4% increase in conductivity of alkali metal solutions at −78° in a field of the order of 15 kv./cm. is attributed to their quasi-metallic nature.[42] The conductivities of the systems sodium–potassium–ammonia and sodium–lithium–ammonia between −70° and −45° have been measured to detect formation of the compound Na_2K and to determine the boundaries of the miscibility gap for $Na–NH_3$ in both systems.[43] A conductance function, which represents the experimental data up to 0·04N., has been derived[44] for dilute sodium solutions. Electrolysis of a solution of aluminium iodide between a platinum cathode and an aluminium anode resulted in a deep blue colour around the cathode; this may be due to formation of aluminium ions and electrons in the solution.[45, 46]

Ogg[47] found that from 10^{-4} to 10^{-3} M. solid solutions of sodium and potassium had a marked positive temperature coefficient of specific resistance in contrast to a negative coefficient for the liquid solutions. Liquid solutions of sodium, 10^{-5} M., in the range −35° to −75°, showed a marked increase in the conductivity upon irradiation with visible light, the quantum efficiency of this effect being an inverse function of concentration.[10] Extremely rapid cooling from −33° to −95° reduced the resistance from 10 kΩ to 16Ω and the solutions were shown to be super-conducting by the classical ring experiment.[48, 49] The effect was not observed with lithium solutions[50] and it was shown that the persistent currents were not due to superconductivity since their direction was not influenced by the direction of a magnetic field.[51] Other workers have been unable to observe this persistent current.[52–59]

The apparent anomalies in the electrical resistance found by Ogg were explained in terms of a supercooled eutectic,[55] but this was considered unlikely by Jaffe,[60] who evoked the idea of a solid compound of sodium and ammonia forming a network throughout solid NH_3. The specific resistance of saturated solutions of sodium is given[58] as 2×10^{-4} ohm per cm. and 5×10^{-4} ohm per cm. at −33·5°C. and 90°K., respectively.

Magnetic Properties

The magnetic susceptibilities of sodium solutions in liquid ammonia have been determined. At 230°K., in a 0·5 M. solution, the atomic susceptibility is equal to that of pure sodium. This value increases in proportion to the dilution until, at 0·0022 M., it has about two-thirds of the paramagnetic susceptiblity which would arise from independent magnets having a $\frac{1}{2}$ unit of spin.[61] A value of one Bohr magneton per atom was calculated[62] for high dilutions. At 78°K. and 195°K. Gibney and Pearson[63] found that the volume magnetic susceptibility changed from $-0{\cdot}6$ to $-0{\cdot}7 \times 10^{-6}$ c.g.s. units, at concentrations of 10^{-4} to 1 mole Na per litre, to about 10^{-7} c.g.s. units at 5 moles Na/litre. Freed and Sugarman[64] have tabulated values for potassium, caesium, calcium and barium. Deigen[65, 66] has developed a theory to explain the magnetic properties of metal–ammonia solutions on the concept of local centres of electrons in an ionic dielectric. Paramagnetic resonances at 19 and 7230 Mc./sec. were found for sodium solutions in the range 0·1 to 0·5 M.[67] Weak-field studies have also been made at low frequencies.[68] Solutions of potassium showed no abnormally large diamagnetism in similar paramagnetic resonance studies.[69, 70] Electron spin resonance studies[71] support the picture of electrons, in equilibrium with respect to the reaction $2\epsilon \rightleftharpoons \epsilon_2 + 0{\cdot}2$ ev., occupying cavities in the liquid, the cavities having a volume of 2 to 4 ammonia molecules. Electron spin resonance measurements at 300 Mc./sec. on frozen metal ammonia solutions have shown[72, 73] that the metal is precipitated out in small particles. Newman and Ogg[74] interpreted their nuclear spin relaxation data from dilute sodium solutions as supporting the idea of an association equilibrium existing between paramagnetic and diamagnetic solute species.

Photoelectric emission studies[75–77] show a change in the long wave threshold from 7700 A. for saturated solutions to about 15,000A. for dilute sodium solutions.[75,76] Ogg[75] assumed this shift to be due to equilibrium between trapped electrons, in pairs and singly. The work function varied from 1·60 to 1·40 ev.[76]

Optical Properties

Solutions of the alkali metals vary from blue for the more dilute to a bronzy metallic lustre at higher concentrations. Earlier work[78, 79] suggested that the solutions were colloidal, but they were later shown[80] not to be so. Ogg[81] showed that when 10^{-3} M. solutions of sodium and magnesium in liquid ammonia are cooled from room temperature to −80° the absorption coefficient of blue light is slightly increased, whilst that for red is doubled. This effect is attributed to a change in the equilibrium concentration of electron pairs and single electrons caused both by temperature and concentration changes. Studies have been made of the absorption spectra of various salts in liquid ammonia[82–84] and Jolly discusses the results in terms of an energy level diagram.[83] Electrolysis of a sodamide solution gives rise to a slow moving, negatively charged blue streak, assumed to be due to electrons immobilized by polarization of the medium (polarons).[85] Deigen[41] explains the peculiarities of the spectra of absorbed light in terms of his concept of metal ammonia solutions as ionic dielectrics and the theory of polarons and single and double colour-centres.

Electrochemical Properties

Pleskov[86] argues that the decomposition potential of liquid ammonia should be about 1/15 of that for water, i.e. 0·08 v., and that for solutions of neutral salts it should be 1·52 v., owing to the formation of acid and alkali at the electrodes. The higher experimental values are due to overvoltage and result in nitrogen being liberated in most salt solutions owing to the more negative potential of the N_2/NH_2^- electrode.[86]

The standard electrode potentials of the alkali and other metals relative to the hydrogen electrode have been given,[87, 88] but Pleskov and Monoszon[89–91] prefer values relative to the lead electrode and have given the following electrode potentials for water (E_{H_2O}) and liquid ammonia (E_{NH_3}):

	Pb	Na	K	H_2
E_{NH_3} volts	0	−2·17	−2·32	−0·34
E_{H_2O} volts	0	−2·58	−2·79	+0·13

Later values[92] based on measurements on the amalgams at −50° were:

	Li	Na	K	Rb	Ca
E_{NH_3} volts	−2·99	−2·59	−2·73	−2·68	−2·39
E_{NH_3}–E_{H_2O} volts	+0·03	+0·12	+0·19	+0·25	+0·38

With the potential of Pb/0·1 N. $Pb(NO_3)_2$ as 0 at −50° the following values were found[25]:

	Zn	Cd	H_2	Cu	Ag	Hg
E_{NH_3} volts (Pb=0)	−0·848	−0·510	−0·331	0·103	0·472	0·414
E_{H_2O} volts (Pb=0)	−0·27	−0·27	0·13	0·47	0·94	0·99

Nickel should probably be placed directly above hydrogen in the electrochemical series.[93] The normal potential of the $Cu:Cu^+$ electrode, calculated from measurements of the e.m.f. of the cell Cu^+/0·1 N. CuI/saturated KNO_3/0·1 N. $Pb(NO_3)_2$/Pb. with liquid ammonia as solvent, is 2·34 v.[94] Between −65° and −35° the e.m.f. of the cells $Pb/Pb(NO_3)_2:AgNO_3/Ag$ and $Cd/Cd(NO_3)_2,4H_2O:AgNO_3/Ag$ are $E=0{\cdot}462+0{\cdot}0005\ (t+35^\circ)$ and $E=0{\cdot}963-0{\cdot}00033\ (t+35^\circ)$ respectively.[95] Other values of the standard electrode potentials of the halogens and metals have been calculated.[96] The cell Zn(amalgam)/$ZnCl_2,10NH_3(s),NH_4Cl$ in $NH_3(l),TlCl(s)$/Tl (amalgam) is reversible and constant in e.m.f. The standard e.m.f. with the Zn and Tl present at unit activity in the amalgams is 0·9016 v. at 25°.[97]

The electrocapillary properties of mercury in liquid ammonia in the presence of a wide variety of organic compounds have been studied.[98, 99] Using 0·1 M. ammonium nitrate as stock electrolyte, their adsorption practically ceased at a polarization of −0·4 v.

Theory of Alkali Metal Solutions

There have been a number of discussions of the state of the electrons in these solutions.[100, 101] Lipscomb[102] calculated that the radius of the spherical cavity occupied by an electron in a solution of sodium is 4·8 A., or slightly less, compared with the experimental value of 3·2 A. The electronic nature of the light absorption centres has been examined.[41, 103–105] Exchange of deuterium with potassium amide, but not with potassium solutions, proves the absence of amide in the latter.[106] The mechanism of the electrical conductance of alkali metal solutions has also been discussed.[107, 108]

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PHYSICAL PROPERTIES OF SOLUTIONS OF SALTS IN LIQUID AMMONIA

Owing to the large number of measurements of various physical properties of salts in liquid ammonia, no attempt has been made to tabulate the results, but a list of references is given in the following Table. References in italics refer to ammonia solutions containing two or more salts. The properties of solutions of salts, and of some other compounds, in liquid ammonia are discussed in the Supplements which deal with the various solutes concerned.

Table XXIV.—The Physical Properties of Solutions of Salts in Liquid Ammonia

	Specific Gravity	Viscosity	Conductivity	Diss. Const. and Ionic Rad.	Activity Coefficient	Surface Tension	Decomposition Voltage	Heats of Solution and Evaporation	Solubility	Vapour Pressure
AgBr	—	—	—	—	—	—	—	64	17, 23, 32	—
AgCl	—	—	—	—	—	—	—	—	17, 23, 32, 34	—
AgF	—	—	—	—	—	—	—	64, 70	17	—
AgI	76	76	—	—	—	—	—	70, 71	17, 23, 32	—
$AgNO_3$	76	76	—	—	—	—	—	—	17, 23	—
$BaBr_2$	—	—	—	—	—	—	—	—	32	—
$BaCl_2$	—	—	—	—	—	—	—	—	23, 30	—
$Ba(ClO_4)_2$	—	—	—	—	—	—	—	—	66	—
$Ba(NO_3)_2$	—	—	—	—	—	—	—	—	23, 29, 32, 38, 39	59
BaI_2	—	—	—	—	—	—	—	—	32	—
$CaBr_2$	—	—	—	—	—	—	—	—	32	—
$Ca(ClO_4)_2$	—	—	—	—	—	—	—	—	66	—
CaI_2	—	—	—	—	—	—	—	72	32	—
$Ca(NO_3)_2$	—	—	—	—	—	—	—	—	29, 32, 38, 39	50, 55
$Cd(NO_3)_2$	—	—	—	—	—	—	—	—	29, 33	—
CsBr	—	—	—	—	—	—	—	—	32	—
CsCl	—	—	—	—	—	—	—	—	32	—
CsI	—	—	—	—	—	—	—	—	32	—
$CsNO_3$	—	4	4, 69	—	—	—	—	—	—	—
$Cu(NO_3)_2,4NH_3$	76	76	—	—	—	—	—	—	—	—
$Cu(OH)_2$	—	—	—	—	—	—	—	—	83	—
H_3BO_3	—	—	—	—	—	—	—	—	23	—
HCN	—	—	—	9	—	—	—	—	—	—
H_2S	—	—	—	9	—	—	—	—	—	—
$Hg(CN)_2$	—	—	—	—	—	—	—	71	—	81
HgI_2	—	—	—	—	—	—	—	62	—	—
KBr	1	—	57	—	—	15	57, 68	70	17, 19, 22, 29, 30, 34, 57	57
$KBrO_3$	—	—	—	—	—	—	—	—	23, 30	—
KCl	1	—	—	—	67	—	—	—	17, 19, 22, *24*, 29, 30, 34, 42	—
$KClO_3$	—	—	—	—	—	—	—	—	23, 30	—
KCN	—	—	—	—	—	—	—	—	34	—
KCNO	—	—	—	—	—	—	—	—	19	—
KCNS	—	—	—	—	—	—	—	65	—	—
K_2CO_3	—	—	—	—	—	—	—	—	19	—
$KC_2H_3O_2$	—	—	—	9	—	—	—	—	34	—
KF	—	—	—	—	—	—	—	—	17, 29	—
KI	1, 76	76	—	—	—	15	68	65, 70	17, 19, 22, 29, 30	—
KIO_3	—	—	—	—	13	—	—	—	*13*, 23, 30	—
KNH_2	—	—	5	—	—	—	—	65	23	—
KNO_3	20, 45	4	4, 6, 7, 69	—	—	—	—	70	17, 19, 20, 22, 26, 29, 30, 42, 45	—
KOH	—	—	—	—	—	—	—	—	17	—
K_2SO_4	—	—	—	—	—	—	—	—	19	—
LiBr	1	—	—	—	—	—	—	62	—	—
LiCl	1	—	—	—	—	—	—	—	30, 32, 34, 58	58
LiC_2H	—	—	86	—	—	—	—	—	—	—
LiF	1	—	—	—	—	—	—	—	17	—
LiI	—	—	—	—	—	—	—	62	—	—
$LiNO_3$	27	4	4, 27 69	—	—	—	27	70	23, 27	52, 82
Li_2SO_4	—	—	—	—	—	—	—	—	23	—
$MgBr_2$	—	—	—	—	—	—	—	—	32	—

	Specific Gravity	Viscosity	Conductivity	Diss. Const. and Ionic Rad.	Activity Coefficient	Surface Tension	Decomposition Voltage	Heats of Solution and Evaporation	Solubility	Vapour Pressure
$Mg(ClO_4)_2$	—	—	—	—	—	—	—	—	66	—
MgI_2	—	—	—	—	—	—	—	—	23, 32	—
$Mg(NO_3)_2$	—	—	—	—	—	—	—	—	29	—
MnI_2	—	—	—	—	—	—	—	—	23	—
NaC_2H	—	—	86	—	—	—	—	—	—	—
$NaC_7H_5O_2$	—	—	—	9	—	—	—	—	—	—
NaCl	1, *2*, 45, *46*, *47*, 60	3	6, 7, 8, 54	—	67	15	—	21, 44, *47*, 61, 63	18, 19, 21, 22, *23*, *24*, 26, *28*, 30, 31, 34, *35*, *37*, *42*, 43, 44, 45, *46*, *47*, 54	43, 44, *47*, 54, 46, 60
$NaClO_3$	—	—	—	—	—	—	—	71	—	—
$Na(CHO_2)$	—	—	—	9	—	—	—	—	—	—
NaCN	—	—	—	—	—	—	—	—	40	—
NaCNO	—	—	—	—	—	—	—	—	48	—
NaCNS	—	—	—	—	—	—	—	—	19, 30, 80	79, 80
$NaC_2H_3O_2$	—	—	—	9	—	—	—	—	—	—
NaF	—	—	—	—	—	—	—	—	19	—
NaI	1	3	—	—	—	—	—	63, 70	18, 19, 22, 30, *74*	—
$NaNH_2$	—	—	5	—	—	—	—	—	23, *28*, *47*	—
$NaNO_3$	60	3, 4	4, 56 69	—	—	—	68	49, 63, 70	18, 19, 22, *23*, 30, *37*, 42	49, 51, 56, 60
NaOH	—	—	—	—	—	—	—	—	41	—
Na_2SO_3	—	—	—	—	—	—	—	—	19	—
Na_2SO_4	—	—	—	—	—	—	—	—	19, 23	—
NH_2OH,HCl	—	—	—	—	—	—	—	65	—	—
NH_4Br	60, 76	76	—	9	11	—	68	62, 70	17, 18, 19, 32, 34	53, 60
NH_4Cl	*2*, 60	3	8	9	10, 11, 12	—	68	25, 47, 62, 70	17, 18, 19, *23*, *24*, 25, 32, 34, *35*, 47	12, 25, 47, 53, 60
NH_4ClO_4	—	—	—	9	—	—	—	—	23	—
NH_4CNS	—	—	—	—	—	—	—	65	19	—
$NH_4C_2H_3O_2$	—	—	—	—	—	—	—	—	23	60
$(NH_4)_2C_2O_4$	—	—	—	—	—	—	—	—	19	—
NH_4F	—	—	—	—	—	—	—	—	17	—
NH_4I	—	—	—	—	11	—	—	63,70	17, 18, 23, 32	53, 60
NH_4HCO_3	—	—	—	—	—	—	—	—	23	—
$(NH_4)_2HPO_4$	—	—	—	—	—	—	—	—	23	—
NH_4NO_3	19, 60	—	—	9	10, 11	—	68	65, 70	17, 18, 19, *23*	53, 55, 60
NH_4N_3	—	—	—	—	—	—	—	—	77	—
$(NH_4)_2S$	—	—	—	—	—	—	—	—	23	—
$(NH_4)_2SO_3$	—	—	—	—	—	—	—	—	19	—
N_2H_4	—	—	—	—	—	—	—	—	—	78
$N_2H_5N_3$	—	—	—	—	—	—	—	—	—	88
PbI_2	—	—	—	—	—	—	—	62, 71	—	—
$Pb(NO_3)_2$	—	—	—	—	—	—	—	71	—	—
RbBr	—	—	—	—	—	—	—	62	32	—
RbCl	—	—	—	—	—	—	—	—	31, 32	—
RbI	—	—	—	—	—	—	—	—	32	—
$RbNO_3$	—	4	4, 69	—	—	—	—	—	—	—
$SrBr_2$	—	—	—	—	—	—	—	—	32	—
$Sr(ClO_4)_2$	—	—	—	—	—	—	—	—	66	—
SrI_2	—	—	—	—	—	—	—	—	32	—
$Sr(NO_3)_2$	—	—	—	—	—	—	—	—	23, 29, 32, 39	59
$Th(C_2O_4)_2,2H_2O$	—	—	—	—	—	—	—	—	84	—
$Th(IO_3)_4$	—	—	—	—	—	—	—	—	84	—
$ZnCl_2$	—	—	—	—	—	—	—	—	—	85
ZnI_2	—	—	—	—	—	—	—	—	23	—
$Zn(NO_3)_2$	—	—	—	—	—	—	—	—	33	—
ZnO	—	—	—	—	—	—	—	—	23	—

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ADSORPTION OF AMMONIA ON SOLIDS

Carbon

Many measurements have been made of the adsorption of ammonia on various forms of carbon.[1–16] Charcoal impregnated with weak acids seems the most efficient absorbent for use in ammonia gas masks.[17] A mixture with anhydrous silica gel, containing 60–70% of charcoal, adsorbs more ammonia than would be adsorbed additively by the gel and charcoal considered separately.[18] At 750–900° ammonia forms a stable nitrogen complex on the surface of charcoal.[19] The presence of oxygen

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complexes on the surface of charcoal increases considerably the adsorption of ammonia at low pressures.[20] Some results obtained at −43°C. at a relative pressure of ammonia of 0·2, before and after evacuation to remove the oxygen complexes, are as follow:

Carbon type	Ammonia adsorbed, c.c./g.	Surface area, m.^{2}/g.	Oxygen content
Spheron 6	39	132	4·2
Spheron 6 after evacuation	15	128	0·9
Black Pearls 1	280	998	1·7
Black Pearls 1 after evacuation	170	860	0·0
Mogul carbon black	130	522	2·2
Mogul carbon black after evacuation	36	184	0·0
Lamp black T	23	28·8	19·1
Lamp black T after evacuation	2	23·5	0·0

The oxygen content of the carbon is expressed as 100 × % of volatile content/surface area per g. which was calculated from the adsorption isotherms.[21]

The calorimetric heat of adsorption of ammonia on Spheron 6 at −78°C. falls from 12 kcal./mole at low coverage to 8–9 kcal./mole. Evacuation at 1000°C. to remove oxygen complexes decreases the heat of adsorption to about 10 kcal./mole at low coverage and 6–7 kcal./mole for coverages from 5–40 c.c./g. Graphitization of the Spheron 6 at 2700°C. further reduces the heat of adsorption to about 6 kcal./mole.[22] On coconut charcoal the heat of adsorption at 0°C. fell from 14·6 kcal./mole at zero coverage to 6·83 kcal./mole at 31 c.c./g.[23] Similar measurements have been made on charcoal[24, 25] and graphite.[26]

The electrical resistance of a rod of active carbon increased by a maximum of 3·1% on adsorption of ammonia.[27] The linear expansion of a rod of willow wood charcoal at −78°C. and −38°C. resulting from adsorption of 25–145 c.c./g. ammonia was 0·1 to 0·45%.[28, 29]

Minerals

The literature on the adsorption of ammonia by minerals is extensive. Studies have been made on analcite,[30–36] apophyllite,[30] asbestos,[37, 38] attapulgite,[39, 40] bentonite,[30, 38, 41–45] chabazite,[34, 35, 46–51] epistilbite,[38] gmelinite,[52] heulandite,[34, 46] inesite,[30] laumontite,[30, 53] leonardite,[13] meerschaum,[54] montmorillonite,[45, 55, 56] mordenite,[30, 38, 51, 52, 57] natrolite,[30, 34] phillipsite,[38] scolecite,[34, 38] sepiolite and serpentine,[38] stilbite,[30] talc, thomsonite and vivianite,[38] fuller's earth,[1] clays[38, 58–62] and a synthetic zeolite.[63] Adsorption by glass,[64–69] silica gel,[8, 14, 50, 69–73] and quartz,[74–76] as well as the heat of adsorption on silica gel[70, 77, 78] were measured. The changes in the dielectric properties of silica gel[79] and rutile[80] due to the adsorption of ammonia have been reported and discussed. An investigation of the absorption spectrum of ammonia adsorbed on silica, with and without added iron, showed that there is a shift in the absorption maximum on a catalytically active surface.[81]

Metals, Oxides and Miscellaneous Adsorbents

Other adsorbents for ammonia that have been studied include copper and copper catalysts,[82] cuprous oxide,[83] iron,[84, 85] an iron catalyst,[86] iron oxide[68, 87] and other oxides and their mixtures,[88] germanium dioxide,[74] alumina,[89] manganese dioxide,[90] oxides of chromium, aluminium, lead, magnesium and calcium,[69] catalysts containing cobalt[91] and nickel,[92] as well as the pure metals nickel[93, 94] and platinum[93, 95] and silica–alumina catalysts.[73, 96] The heats of adsorption of ammonia, as a function of surface coverage, on evaporated films of nickel, iron and tungsten were obtained calorimetrically.[97] Other miscellaneous adsorbents studied were potassium benzenesulphonate,[98] arsenic trisulphide,[99] lignite,[13, 100] titania,[101, 103] oxides of tin, cerium and thallium,[103] sapphire,[104] sodium chloride,[104, 105] ammonium chloride,[106] barium fluoride,[107, 108] magnesium perchlorate,[109] wood and cellulose,[110] silk fibroin[111] and egg albumin.[112] Three papers describe the adsorption of ammonia on oriented films of palmitic acid; desorption occurs without heating.[113–115] The heat of adsorption on zinc oxide has been determined calorimetrically.[116]

Heats of Adsorption

The variation of the heat of adsorption of ammonia with coverage on a non-conducting surface has been calculated taking account of van der Waals forces and the change of dipole moment with coverage. These effects are of the same order of magnitude and of opposite sign; hence the resultant variation is small.[117] On a number of solids the heat of adsorption is about equal to the heat of sublimation,[118] but activated adsorptions and desorptions of ammonia are also observed.[119] The cross-sectional area of the adsorbed ammonia molecule is 14·6 A.^{2} at -32°C. if it is assumed that the area of the nitrogen molecule is 15·4 A.^{2} at -196°C.[120] The maximum reversible change of surface electrical potential on adsorption of ammonia at room temperature is $+150$ millivolts for a paraffin surface and -100 millivolts for a collodion surface.[121]

The isosteric heats of adsorption of ammonia are 14·4 kcal./mole on sodium chloride, 11·4 kcal./mole on potassium chloride, 13·2 kcal./mole on rubidium chloride, 15·3 kcal./mole on potassium iodide, 24·6 kcal./mole on barium chloride and 29·3 kcal./mole on calcium fluoride.[122, 123] On both molybdenum silicide and tungsten silicide the value 26 kcal./mole is obtained for non-activated adsorption and more than 40 kcal./mole for activated absorption.[124] These values of the heat of adsorption are related to the hardness and reactivity of the solid.[124, 125]

The kinetics of adsorption of ammonia by dehydrated potash alum were interpreted on the basis of two different categories of adsorption sites.[126]

The permeabilities of polyethylene and trifluoromonochloroethylene to ammonia increase exponentially with temperature; at 25°C. values are $2{\cdot}5 \times 10^{-9}$ and $0{\cdot}5 \times 10^{-9}$ respectively, and at 50°C. 11×10^{-9} and $1{\cdot}6 \times 10^{-9}$ respectively, the units being c.c. of ammonia at N.T.P. passing through 1 cm.^{2} of film, 1 cm. thick, per sec., per cm. of mercury pressure difference.[127] Measurements have been made also with collodion[128] and of the relative permeabilities of rubber, gelatin and celluloid.[129]

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PHYSICAL PROPERTIES OF AMMONIUM HYDROXIDE

Composition

The extent to which aqueous ammonia exists as NH_4OH or as hydrated NH_3 has long been discussed (Mellor, VIII, 188, 195). Measurements of the vapour pressure and electrical conductivity,[1] the pH of ammonium salts[2] and the distribution of ammonia between water and dichloroethane[3] indicate that the ammonia is present largely as NH_4OH. However, on the basis of the Raman spectrum, the infra-red spectrum and thermochemical data, some authors have concluded that NH_4OH is not formed.[4–6] Thus the heat of formation of gaseous NH_4OH from NH_3 and H_2O has been calculated as -49 or -74 kcal. (according to whether the intramolecular distance is assumed to be 2·5 or 3), and that of aqueous NH_4OH as -30 to -50 kcal.,[4] whilst the measured heat of the reaction: $NH_3(g)+H_2O(l) \rightarrow NH_4{}^+aq+OH^-aq$, is only 6·5 kcal. Proton magnetic resonance of aqueous ammonia at various concentrations gives a single absorption line, indicating that not more than one species exists with a lifetime longer than about 10^{-3} sec. A fast proton exchange is inferred; there are significant interactions between NH_3 and H_2O, but the state is a very dynamic one and the description of the molecule as either NH_4OH or NH_3,H_2O is somewhat arbitrary.

Solid Hydrates of Ammonia

The phase diagram of the ammonia–water system shows three eutectics: $-101{\cdot}3$°C. at 32·7% NH_3, $-85{\cdot}4$°C. at 56·7% NH_3 and $-92{\cdot}2$°C. at 79·9% NH_3, and two compounds: NH_3,H_2O m.p. $-77{\cdot}0$°C. and $2NH_3,H_2O$ m.p. $-77{\cdot}4$°C.[8, 9] This agrees with the results of Rupert (Mellor, VIII, 194). Comparison with the ammonia–acetic acid system indicates the enormous difference in stability of the addition compounds formed in the two cases; this is a consequence of the much greater tendency of acetic acid to act as a proton donor as compared with water.[10]

Hildenbrand and Giauque[11] made a calorimetric study of the hydrates of ammonia from 15°K. to 290°K.; the thermodynamic properties obtained are given in Tables XXV and XXVI.

Table XXV.—Thermodynamic Properties of Ammonium Oxide, $(NH_3)_2,H_2O$. g.-cal. $mole^{-1}$ $deg.^{-1}$

Temperature, °K.	C_p	S	$(H^\circ-H_0^\circ)/T$	$-(F^\circ-H_0^\circ)/T$
15	1·085	0·394	0·291	0·103
30	4·649	2·177	1·534	0·643
50	12·032	6·012	4·039	1·973
100	16·592	15·417	8·895	6·522
150	22·485	23·301	12·477	10·824
194·32 melting point				
200	47·552	43·168	27·962	15·206
250	52·617	54·337	32·400	21·937
298·16	56·355	63·942	35·983	27·959

Table XXVI.—Thermodynamic Properties of Ammonium Hydroxide, NH_3,H_2O. g.-cal. $mole^{-1}$ $deg.^{-1}$

Temperature, °K.	C_p	S	$(H^\circ-H_0^\circ)/T$	$-(F^\circ-H_0^\circ)/T$
15	0·419	0·140	0·104	0·036
30	2·185	0·933	0·675	0·258
50	4·845	2·679	1·818	0·861
100	10·643	7·891	4·836	3·055
150	15·441	13·137	7·591	5·546
194·15 melting point				
200	28·566	26·530	18·210	8·320
250	33·081	33·391	20·734	12·657
298·16	37·022	39·567	23·057	16·510

The heat of fusion of ammonium hydroxide is 2352 g.-cal./mole and its density at 205°K. is 0·89 g./c.c. The heat of fusion of ammonium oxide is 1568 g.-cal./mole and its density 0·82 g./c.c. C_p for ammonium oxide shows two sharp maxima near

52°K. which are typical of co-operative phenomena and are believed to be due to angular motions of the NH_4 groups.

The heat of the reaction

$$NH_3(g) + NH_4OH(l) = (NH_4)_2O(l)$$

was found to be $\Delta H^\circ_{25} = +5598$ g.-cal. mole^{-1}.

The entropies of the reactions:

$$NH_3(g) + H_2O(l) = NH_4OH(l) \quad \text{and} \quad NH_3(g) + NH_4OH(l) = (NH_4)_2O(l)$$

calculated from the Third Law of Thermodynamics, were found to agree closely with values for the ammonia–water system and ammonia; thus all hydrogen bonds and other structural details of crystalline ammonium hydroxide and ammonium oxide must be essentially ordered at low temperatures.[11, 12]

X-Ray examination showed ammonium hydroxide at −95°C. to be hexagonal with $a = 11{\cdot}21 \pm 0{\cdot}05$ A. and $c = 4{\cdot}53 \pm 0{\cdot}02$ A.[13] Ammonium oxide is orthorhombic; space group *Pbnm*. The unit cell contains 4 molecules and has the dimensions $a = b = 8{\cdot}41 \pm 0{\cdot}03$ A., $c = 5{\cdot}33 \pm 0{\cdot}02$ A. The structure contains planar chains of alternating NH_3 and H_2O molecules bonded by hydrogen bonds of the O–H. . .N and N–H. . .O types. The chains are cross-linked into a three-dimensional network by hydrogen bonds of the latter type. Half of the ammonia molecules are not part of this network, but are attached to it by single hydrogen bonds, about which they are presumably free to rotate.[13]

Electrical Conductivity

Values for the electrical conductivity of aqueous ammonia are given in Tables XXVII[1] and XXVIII.[14] Table XXVII includes also values of the partial pressure of ammonia.

Table XXVII.—Specific Conductivity of Aqueous Ammonia

Temperature, °C.	%NH_3	Specific conductivity × 10^4 mhos.	Partial pressure of NH_3, cm. Hg
0	0·419	2·721	0·15
	1·072	4·167	0·29
	6·241	6·421	1·43
	10·56	5·584	2·72
	19·76	2·791	7·75
	28·58	1·138	17·71
	35·60	0·488	32·18
25	0·404	5·290	0·31
	1·042	8·207	0·84
	5·259	12·75	4·43
	9·517	11·42	9·09
	18·61	6·254	24·56
	27·20	2·857	51·63
	30·97	1·965	68·67

Table XXVIII.—Specific Conductivity of Aqueous Ammonia × 10^6 in mhos

Temperature, °C. %NH_3	−30	−20	−10	0	10	20	30
26·0	30·5	53·6	87·0	133·7	191·0	260·5	341·3
30·0	19·6	34·9	57·3	88·3	128·1	176·5	233·0
35·6	10·0	18·0	29·9	46·6	68·4	95·7	128·7
42·6	5·3	9·4	15·5	24·2	35·6	49·7	67·2
48·9	3·3	5·6	8·9	13·7	20·1	28·6	40·7
58·5	1·7	2·6	4·0	5·8	8·3	12·0	16·8
72·3	6·1	7·7	9·6	12·4	15·0	18·6	23·8
100	2·5	2·9	3·5	4·0	4·4	5·0	—

At high field strengths the conductivity of aqueous ammonia is increased (the Wien effect).[15–20] Thus for 0·031 M. NH_3 the increase is 12·5% at 240 kv./cm.[15] The results have been used to calculate the proportion of the ammonia that is present as NH_4OH.[16] The dissociation field effect shows a dispersion in the range of 1 microsec. from which the following rate constants can be calculated.[18, 19]

$$NH_4^+ + OH^- \rightarrow NH_3,H_2O \qquad k_1 \approx 3 \times 10^{10}\ \text{l mol.}^{-1}\ \text{sec.}^{-1}$$

$$NH_3,H_2O \rightarrow NH_4^+ + OH^- \qquad k_2 \approx 5 \times 10^{5}\ \text{sec.}^{-1}$$

The breakdown voltage of 0·05 N. NH_4OH between needle electrodes, 0·4–2·4 mm. apart, is 25–38 kv.[21]

The conductivity of aqueous ammonia at a frequency of 43·9 Mc./sec. is the same as that at low frequencies.[22] The conductivities of dilute solutions of ammonia in methanol, ethanol and both propanols have been measured in the temperature range −10° to 40°C.; minima are observed on plotting conductivity against temperature.[23, 24] From measurements of the conductivity, at 25°C., of solutions of ammonia in methanol and ethanol, dissociation constants for ammonia of 2×10^{-6} and $1{\cdot}5 \times 10^{-7}$, respectively, are obtained.[25]

The conductivity of aqueous ammonia increases with increase in pressure.[26] Some measurements are given in Table XXIX[27] and Table XXX[28] together with values of the basic ionization constants of ammonia calculated from the conductivities.

Table XXIX.—Molar Conductances of Ammonia in mhos

Pressure, atm.	1	1	1000	1000	2000	2000	3000	3000
Temp., °C.	25	45	25	45	25	45	25	45
Concentration (moles/1000 g.)								
0·001	34·7	48·8	58·8	79·0	86·5	112·4	115·8	148·8
0·004	17·5	24·4	31·2	41·0	47·7	61·3	66·8	84·3
0·010	11·4	16·0	20·3	26·9	31·7	40·7	45·0	57·1
0·106	3·52	4·86	6·37	8·34	10·17	12·98	14·63	18·63
$K \times 10^5$	1·75	1·81	5·11	4·79	12·2	11·1	24·3	22·3

Table XXX.—Molal Conductance and Ionization Constant of 0·01093 *Molal Ammonia at* 45° *C.*

Pressure, atm.	1	1100	2500	4000	5400	6800	9600	12,000
Molal conductance	14·9	25	49	83	115	151	214	248
$K \times 10^5$ mhos	1·93	5·03	18·2	48	113	211	620	1010

Ionization Constant of Ammonium Hydroxide

The most reliable values are obtained by combining the ionic product of water with the dissociation constant of the ammonium ion obtained by an e.m.f. method, the Debye–Hückel theory being used to extrapolate the results to zero ionic strength. Bates and Pinching[29] obtained $K_b = 1{\cdot}37 \times 10^{-5}$, $1{\cdot}77 \times 10^{-5}$ and $1{\cdot}89 \times 10^{-5}$ at 0°, 25° and 50°C., respectively, using the cell:

$$Pt,H_2/NH_3(m),NH_4Cl(m)/AgCl,Ag$$

and the same values using the cell:

$$Pt,H_2/NH_3(m)K\ H\ \text{phenolsulphonate}\ (m)/AgCl,Ag$$

in conjunction with the dissociation constant of phenolsulphonic acid.[30] Everett and Landsman[31] obtained $K_b = 1{\cdot}76 \times 10^{-5}$ at 25°C. using the cell:

$$Pt,H_2/NH_3,NH_4Cl,KCl/3{\cdot}5\ \text{N.}\ KCl/HCl,KCl/H_2,Pt.$$

A previous determination by the same method[32] gave the low value of $1\cdot65\times10^{-5}$, probably because of the presence of carbonate in the hydroxide solution used in preparing the buffer solutions.

From the temperature coefficient of the dissociation constant of the ammonium ion the thermodynamic functions for the reaction:

$$NH_4^+,\ aq. = H^+,\ aq. + NH_3,\ aq$$

given in Table XXXI are calculated.

Table XXXI.—Thermodynamic Functions for the Dissociation of the Ammonium Ion

	K_a (298·16°)	$\Delta G^\circ_{298\cdot16}$ g.-cal. mole^{-1}	$\Delta H^\circ_{298\cdot16}$ g.-cal. mole^{-1}
Bates & Pinching[29]	$5\cdot69\times10^{-10}$	$12{,}611\pm1\cdot5$	$12{,}478\pm70$
Everett & Landsman[31]	$5\cdot77\times10^{-10}$	$12{,}606\pm2\cdot0$	$12{,}380\pm75$
		$\Delta S^\circ_{298\cdot16}$ g. cal. deg.$^{-1}$mole^{-1}	$\Delta C_p{}^\circ_{298\cdot16}$ g.-cal. deg.$^{-1}$ mole^{-1}
		$-0\cdot45\pm0\cdot2$	0
		$-0\cdot75\pm0\cdot25$	0

The apparent ionization constant of ammonia at high salt concentrations has been measured[33, 34] as well as the dissociation constant of the ammonium ion in 60% aqueous methanol.[35]

The heat of ionization of ammonium hydroxide determined calorimetrically is $\Delta H^\circ_{298\cdot16}=865$ g.-cal./mole^{-1}.[36]

Measurements have been made of the effect of varying the temperature[37] and pressure[38] and of illumination[39] on the pH value of ammonia solutions.

Faraday Effect

From measurements of the magnetic rotation of the plane of polarization, at 0°C., for a wave-length 5460 A. using a solution containing 1 mole of NH_4OH in 17 moles of water, a value of 0·0160 was obtained for Verdet's constant and the molecular rotation constant was found to be 3·00.[40]

Viscosity

Table XXXII gives values of the viscosity of aqueous ammonia in centipoises.[41] Other less extensive results are in fair agreement.[42, 43]

Table XXXII.—Viscosity of Aqueous Ammonia in Centipoises

Concentration, %NH_3	8·8	19·6	30·82	39·6	49·3	89·4	100
Temperature, °C.							
−26	—	—	—	—	—	—	0·230
−10	—	—	—	—	—	—	0·183
−4	—	—	—	—	—	—	0·170
10	1·435	1·632	1·695	1·612	1·290	0·239	0·152
30	0·852	0·981	1·034	0·910	0·708	0·187	0·138
50	0·596	0·608	0·615	0·549	0·446	0·144	0·125
70	0·407	0·424	0·432	0·393	0·338	—	—
90	0·313	0·320	0·323	0·298	0·251	—	—
110	0·252	0·258	0·253	0·238	—	—	—
130	0·212	0·206	0·204	—	—	—	—
150	0·178	—	—	—	—	—	—

Density and Surface Tension of Aqueous Ammonia

Table XXXIII gives some measurements of the density and surface tension of aqueous ammonia at 20°C.[44]

Table XXXIII.—Density and Surface Tension of Aqueous Ammonia at 20°C.

Wt.-% of NH_3	Moles of NH_3/litre	Density, g./ml.	Surface tension, dynes/cm.
100	35·836	0·61029	22·03
90·81	34·826	0·6531	24·57
80·95	33·198	0·6984	28·11
70·47	30·799	0·7443	32·99
61·16	28·192	0·7850	37·90
47·45	23·302	0·8363	46·42
29·70	15·504	0·8890	55·58
14·61	8·072	0·9409	62·15
7·72	4·378	0·9661	65·74
0·45	0·264	0·9960	72·55

The surface tension of pure ammonia at 0°C. is 26·43 dynes/cm. and at 10°C. 24·28 dynes/cm.[44]

Interfacial tensions between dilute solutions of palmitic acid in benzene and dilute aqueous solutions of ammonia have been measured.[45]

Vapour Pressure and Solubility

Vapour pressures and vapour compositions were determined for aqueous ammonia from 60° to 150°C.[46] These data were combined with those of Perman and of Mollier (Mellor, VIII, 195) to construct isobars and isotherms from which the values in Tables XXXIV and XXXV were obtained.

Table XXXIV.—Ammonia Concentrations in the Liquid and Vapour Phases at Different Temperatures and Total Vapour Pressures

Total pressure, atm.	10		6		2		1		0.2	
Temperature, °C.	Liquid	Vapour	Liquid	Vapour	Liquid	Vapour	Liquid	Vapour	Liquid	Vapour
160	6·6	36·3	—	—	—	—	—	—	—	—
140	14·0	64·8	5·9	40·0	—	—	—	—	—	—
120	22·0	81·1	13·5	69·9	0·15	1·5	—	—	—	—
100	30·8	91·7	22·0	84·8	6·2	50·6	0	0	—	—
80	40·6	97·4	31·4	94·2	14·0	80·3	6·1	52·6	—	—
60	52·2	—	41·9	—	23·4	94·8	14·4	82·5	—	—
40	70·2	—	54·0	—	33·7	98·4	24·0	94·5	5·5	65·5
25·3	100	100	—	—	—	—	—	—	—	—
20	—	—	74·6	—	45·6	—	34·6	98·5	15·0	90·5
9·7	—	—	100	100	—	—	—	—	—	—
0	—	—	—	—	61·4	—	47·3	—	25·3	98·0
−18·5	—	—	—	—	100	100	—	—	—	—
−20	—	—	—	—	—	—	65·4	—	—	—
−33·2	—	—	—	—	—	—	100	100	—	—
−61	—	—	—	—	—	—	—	—	100	100

Table XXXV.—Ammonia Concentrations in the Vapour Phase and Total Vapour Pressures at Different Liquid Concentrations and Temperatures

Temperature, °C.	60		80		100		120		140	
Liquid Concentration, % NH_3	Vapour %NH_3	Pressure atm.	Vapour %NH_3	Pressure atm.	Vapour %NH_3	Pressure atm.	Vapour %NH_3	Pressure atm.	Vapour %NH_3	Pressure atm.
0	0	0·197	0	0·467	0	1·00	0	1·96	0	3·57
5	56·4	0·439	47·8	0·90	45·6	1·82	39·2	3·22	34·7	5·55
10	75·8	0·717	69·9	1·48	64·5	2·75	60·0	4·70	53·8	7·83
15	84·1	1·084	81·2	2·19	75·3	3·88	72·7	6·55	67·2	10·70
20	91·3	1·559	87·0	3·05	82·8	5·31	79·2	8·83	75·7	14·37
25	—	—	90·8	4·14	87·9	7·18	83·2	11·72	—	19·20
30	—	—	93·3	5·55	91·3	9·48	—	15·46	—	—

Wucherer[47] made similar measurements for 0 to 100% of aqueous NH_3 over the range −50° to 210°C. and 0·1 to 20 atm. The partial pressure of ammonia is given by the empirical equation[48]:

$$\log_{10} p = \frac{7{\cdot}6468t+540{\cdot}85}{t+230} - \frac{0{\cdot}7486t+236{\cdot}68}{t+230} \times \log_{10}\left(\frac{1000}{c} - 1.6\right)$$

where p = partial pressure of NH_3 in mm.,
t = temperature in °C.,
c = concentration of NH_3 in g. of NH_3/1000 g. of solution.

Nomographs[49, 50] and charts[51–53] have been prepared which relate the pressure, composition and temperature of aqueous ammonia solutions.

Measurements of the vapour pressure of ammonia or the solubility of ammonia have also been made for the systems in Table XXXVI.

Table XXXVI.—Vapour Pressure and Solubility of Ammonia in Various Systems

System	References
NH_3, N_2H_4	54, 55
NH_3, aniline	56
NH_3. C_2H_5OH	57
NH_3, NH_4CNS	58
NH_3, H_2O, NaCl	59
NH_3, H_2O, NaCl, CO_2	60–63
NH_3, H_2O, NaCl, $CaCl_2$	64
NH_3, H_2O, $MgCl_2$	65
NH_3, H_2O, H_3PO_4	66
NH_3, H_2O, NaOH	67
NH_3, H_2O, NH_4NO_3	68–70
NH_3, H_2O, NH_4NO_3, CO_2	71
NH_3, H_2O, NH_4Cl, CO_2	72, 75
NH_3, H_2O, $(NH_4)_2SO_4$, CO_2	72
NH_3, H_2O, Cu NH_4 formate, CO_2	73, 74
NH_3, H_2O, CO_2	75–81
NH_3, H_2O, CO_2, H_2S	75, 77, 82, 83
NH_3, H_2O, CO_2, H_2S, K_2CO_3	82
NH_3, H_2O, SO_2	84–89
NH_3, H_2O, urea	70
NH_3. H_2O, urea, CO_2	90

Bell obtained the following values for the solubility of ammonia in c.c. of NH_3 gas at 760° mm. and 20°C. per c.c. of solution[91, 92]: hexane 4·16, octane 2·56, dodecane

2·13, cetane 1·84, carbon tetrachloride 7·17, benzene 9·95, toluene 7·23, chloroform 69·8, bromobenzene 8·08, chlorobenzene 11·35, benzyl chloride 12·30, ethylene chloride 26·6.

Distribution coefficients of ammonia between water and benzene,[3] toluene,[3] dichloroethane,[3] 2-methyl-l-propanol,[93] 1-pentanol[93] and chloroform[94] have been determined. The distribution of ammonia between solid salt ammoniates and chloroform has been used to determine the dissociation pressure of the ammoniate.[95]

Phase diagrams or solubility data have been obtained for the systems listed in Table XXXVII.

Table XXXVII.—Phase Diagrams and Solubility Data in Systems containing Aqueous Ammonia

System	References	System	References
NH_3, H_2O, NaCl	96–99	NH_3, H_2O, $ZnSO_4$	121
,, ,, NaBr	96	,, ,, $Ni(OH)_2$	118, 119, 122
,, ,, NaI	96	,, ,, $Co(OH)_2$	118, 119
,, ,, $NaNO_3$	97, 100	,, ,, $CoCl_2$	123
,, ,, Na_2CO_3	100–103	,, ,, $Cu(OH)_2$	118, 119, 124–126
,, ,, Na_2SO_4	98, 103–106	,, ,, Ga_2O_3	127
,, ,, NaOH	107–108	,, ,, $CdCl_2$	128
,, ,, KCl	97, 98, 100	,, ,, $Cd(NO_3)_2$	129
,, ,, KNO_3	97	,, ,, $CdSO_4$	130
,, ,, K_2CO_3	103,109	,, ,, NH_4ClO_4	117
,, ,, K_2SO_4	98, 103	,, ,, $(NH_4)_2SO_4$	103, 105
,, ,, KOH	108, 110	,, ,, HCl	131
,, ,, AgCl	111, 112	,, ,, N_2O_5	132
,, ,, AgBr	113	,, ,, CO_2	103, 133–137
,, ,, AgCNS	114	,, ,, SO_2	138, 139
,, ,, $AgBrO_3$	115	,, ,, CO_2, NaCl	140, 142
,, ,, $AgIO_3$	111, 115	,, ,, CO_2, Na_2SO_4	143
,, ,, Ag_2SO_4	115	,, ,, CO_2, $(NH_4)_2SO_4$	144, 145, 146
,, ,, Ag_2O	112	,, ,, KCl, KNO_3	147
,, ,, Ag_2Se	116	,, ,, NH_4Cl, NH_4NO_3	147
,, ,, Ag_2Te	116	,, ,, $NH(SO_3NH_4)_2$	148
,, ,, $Ca(OH)_2$	117		
,, ,, $Ca(IO_3)_2$	117		
,, ,, $Zn(OH)_2$	118–120		

Absorption and Desorption

Studies have been made of the absorption of ammonia from air by water in packed towers,[149–156] wetted wall columns[157–159]/disc columns,[160] spray towers,[161, 126] water drops,[163, 164] bubble cap columns[165] and bubbles.[166, 167] The absorption of ammonia from air by aqueous acids in packed towers,[150] wetted wall columns,[159, 168] liquid drops[169] and stirred vessels[170] has also been studied.

The theory of the absorption of ammonia by water[171–176] and by aqueous acids[174, 177, 178] has been developed. In both cases the rate of absorption is mainly determined by the resistance of the gaseous film.

Measurements have been made of the simultaneous absorption of ammonia and carbon dioxide by water[179–181] and of the desorption of ammonia from aqueous solutions.[159, 182–186] The desorption rate is increased by stirring[182] or raising the pH to at least 9[185] and is decreased by the presence of cetyl alcohol which forms a surface film of poor permeability.[184]

The absorption and recovery of ammonia from fuel gases has already been described (see page 242).

Thermodynamic Properties

Zinner[187] measured the heat content of mixtures of 0–100% of ammonia and water over the temperature range −70° to 180°C. These data were combined with the vapour pressure measurements of Wucherer[47] and Perman (Mellor, VIII, 195) to obtain values of the total pressure, the weight fraction of ammonia in the saturated vapour and various thermodynamic properties, some of which are given in Tables XXXVIII to XL[188]; the values given refer to the liquid in equilibrium with its vapour only. The standard state of zero enthalpy and entropy for pure ammonia or for water is the liquid in equilibrium with its own vapour at 32°F.

Table XXXVIII.—Enthalpy (in B.Th.U./lb.) of Liquid Mixtures of Ammonia and Water

Wt. fraction of NH_3 in the liquid	0	0·2	0·4	0·6	0·8	1·0
Temperature, °F.						
−60	—	—	−202·3	−197·4	−158·7	−99·1
0	—	−98·1	−140·7	−135·2	−95·0	−35·0
50	18·0	−46·6	−88·3	−81·8	−40·4	20·0
100	68·0	5·6	−34·2	−26·2	16·7	77·3
150	117·9	59·0	23·3	33·2	76·5	—
200	168·0	115·0	86·9	—	—	—
300	269·6	248·7	—	—	—	—

Table XXXIX.—Entropy (in B.Th.U./lb.°F.) of Liquid Mixtures of Ammonia and Water

Wt. fraction of NH_3	0	0·2	0·4	0·6	0·8	1·0
Temperature, °F.						
−60	—	—	−0·3123	−0·3055	−0·2617	−0·225
0	—	−0·1029	−0·1380	−0·1381	−0·1001	−0·0733
50	0·0361	0·0176	−0·0182	−0·0154	0·0161	0·0397
100	0·1295	0·1154	0·0821	0·0886	0·1215	0·1458
150	0·2149	0·2057	0·1804	0·1881	0·2219	—
200	0·2938	0·2931	0·2769	—	—	—
300	0·4369	0·4743	—	—	—	—

Table XL.—Free Energy (in B.Th.U./lb.) of Liquid Mixtures of Ammonia and Water

Wt. fraction of NH_3	0	0·2	0·4	0·6	0·8	1·0
Temperature, °F.						
−60	—	—	−77·5	−75·3	−54·1	−10·2
0	—	−50·8	−77·2	−74·6	−48·9	−1·2
50	−0·4	−55·6	−79·0	−74·0	−48·6	−0·2
100	−4·5	−58·9	−80·1	−75·9	−51·3	−4·3
150	−13·1	−66·4	−86·7	−81·5	−58·8	—
200	−25·9	−78·4	−95·7	—	—	—
300	−62·3	−111·6	—	—	—	—

Other tables give values of the enthalpy, entropy and free energy of the saturated vapour.[188] Similar compilations of thermodynamic data for ammonia–water mixtures have been made by other authors.[189–192]

The heat of solution of 1 mole of ammonia in 400 moles of water is 8·43 kcal.[193]

Equations have been derived for calculating the heat capacity and specific gravity for various ammonia–salt solutions,[194] and the volume change on ionization of ammonium hydroxide has been determined.[195]

Refs. p. 321

Activity Coefficients

The ionic activity coefficients of 0·5 M. ammonium hydroxide in sodium chloride, potassium chloride, and lithium chloride solutions of various concentrations up to 3 M., determined from e.m.f. measurements of suitable cells, decrease to values of 0·519, 0·591 and 0·373 respectively in 3 M. solutions.[196] Ionic activity coefficients have been obtained also from measurements of electrical conductivity.[197]

The influence of ammonium chloride on the activity of ammonia in aqueous solution was calculated from the distribution of ammonia between chloroform and ammonium chloride solutions.[198] Low concentrations of ammonium chloride reduce the activity coefficient, whereas at higher concentrations the activity coefficient is increased. The distribution of ammonia between toluene and aqueous silver ammonia chloride and hydroxide was used to calculate the activity coefficients of ammonia in the aqueous solutions.[199]

Adsorption

The adsorption of ammonium hydroxide on silica gel is chiefly ionic; the amount absorbed at 25°C. increases from 0·52 milli-equivalents per g. for a final ammonia concentration of 0·0068 N. to 2·14 milli-equivalents per g. at 0·49 N.[200] Acidic hydroxyl groups are responsible for the chemisorption of ammonium hydroxide on quartz, the adsorption capacity of which is 0·013 milli-equivalents per g. having surface area 9000 sq. cm.[201, 202] The adsorption of ammonium hydroxide by alumina from weak solutions is greater at high than at low pH values.[203] On sugar charcoal the extent of adsorption depends on the temperature of activation falling from 2·0 milli-equivalents per g. for charcoal activated at 420°C. to zero for charcoal activated at 850°C. In contrast adsorption of acids is promoted by increase in temperature of activation.[204] Adsorption of ammonium hydroxide at 30°C. on animal carbon is increased by the presence of sodium chloride, potassium chloride or lithium chloride.[205] The ion-exchange resin Amberlite 1 R–100 adsorbs 4·31 milli-equivalents of ammonium hydroxide per g. at an equilibrium concentration of 0·27 N.[206] The adsorption of ammonium hydroxide has been measured on silica, ferric oxide, alumina and various mixtures of silica and ferric oxide or alumina.[207] Adsorption of ammonium hydroxide stabilizes various negative sols against precipitation by electrolytes.[208] The permeability of polythene to ammonium hydroxide has been measured.[209]

Isotope Exchange

The equilibrium constant for the exchange reaction:

$$^{14}NH_4^+ \text{ (soln)} + {}^{15}NH_3 \text{ (gas)} \rightleftharpoons {}^{15}NH_4^+ \text{ (soln)} + {}^{14}NH_3 \text{ (gas)}$$

is 1·034 at 25°C. The constant for the reaction:

$$^{14}NH_3 \text{ (soln)} + {}^{15}NH_3 \text{ (gas)} \rightleftharpoons {}^{15}NH_3 \text{ (soln)} + {}^{14}NH_3 \text{ (gas)}$$

is 1·005 at 25°C.[210]

The mole-% of $^{15}NH_3$ in aqueous ammonia may increase to 74% by adsorption on a sulphonated cation exchange resin followed by elution with sodium hydroxide.[211]

Equilibrium constants for the distribution of deuterium between ammonia and water and the ammonium ion and water have been measured.[212, 213]

Sound Absorption

The absorption of sound by ammonium hydroxide solutions varies linearly with frequency in the range 2–15 Mc./sec.[214]

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PHYSICAL PROPERTIES OF THE AMMONIUM ION

The radius of the aqueous ammonium ion is given as 1·40 ± 0·03 A.,[1] 1·33 or 1·45 A.[2] and 1·333 A.[3] The apparent volume of the ammonium ion in infinitely dilute aqueous solution is 17·7 c.c./g.-ion at 15°C., 18·0 c.c./g.-ion at 25°C., and 18·1 c.c./g.-ion at 35°C.[4] The increase in volume on solution of the ammonium ion is 10 c.c./g.-ion.[5]

The electronic polarizability of the ammonium ion in aqueous solution has been given as 1·618 or 1·532[2] and in ammonium halide crystals as 2·0.[6] The g-ionic diamagnetic susceptibility of the ammonium ion with a co-ordination number of 8 in the crystalline state is $-13{\cdot}7 \times 10^{-6}$ c.g.s. units, with a co-ordination number of 6 $-13{\cdot}8 \times 10^{-6}$ c.g.s. units, and in aqueous solution it is $-14{\cdot}2 \times 10^{-6}$ c.g.s. units.[7] Other values obtained for the susceptibility are $-13{\cdot}3 \times 10^{-6}$, $-13{\cdot}8 \times 10^{-6}$ and $-13{\cdot}4 \times 10^{-6}$ c.g.s. units.[8–11] The molecular magnetorotation constant of the ammonium ion is $2{\cdot}01 \times 10^{-14}$ [12] and the molecular rotation is 88×10^{-6} radians.[13] The shift in the nuclear magnetic resonance frequency of ^{14}N in NH_4^+ compared with NO_3^- is $-1{\cdot}0$ kilocycles with a field of 10,500 gauss.[14]

The conductance of the ammonium ion in 0·01 M. aqueous solution is 69·33 mhos at 25°C.[15] The mobility of ammonium ions in various solutions has been measured.[16–19] From the self-diffusion coefficient it has been calculated that 11·6 hydrogen bonds are formed by each ammonium ion.[20]

The ammonium ion is discharged reversibly at the dropping mercury electrode,[21–23] but concentration polarization is observed with a stationary mercury cathode.[24]

Quantum mechanical treatments of the ammonium ion have given $-17{\cdot}9 \times 10^{-6}$ c.g.s. units for the diamagnetic susceptibility[65] and values for the bond length of 1·02 A., 0·85 A. and 0·97 A.[65–67] compared with an observed value of 1·03 A. in ND_4Cl[67] and 1·03 A. and 1·02 A. for the bond lengths in NH_4^+ and ND_4^+, respectively, calculated from the Raman spectrum.[18] Values of $5{\cdot}38 \times 10^5$ and $5{\cdot}495 \times 10^5$ dyne/cm. have been calculated for the bond stretching force constant of the ammonium ion from spectroscopic data.[68, 69]

The exchange of ammonium ion with other cations has been studied on various synthetic resins,[25–46] on chabazite,[47–49] vermiculite[50, 51] and various clay minerals,[52–58] on soil,[59] glass,[60] coal,[61] silica–alumina gels[62] and sulfocarbon.[63] The mobility of the ammonium ion in a sulfonated resin has been calculated from the electrical conductivity.[64]

Thermodynamic Properties of the Ammonium Ion

The thermodynamic functions C_p°, $(H^\circ - H_0^\circ)/T$, $-(F^\circ - H_0^\circ)/T$, and S° for the ammonium ion in the ideal gas state have been calculated by the rigid rotator-harmonic oscillator approximation from structural and spectroscopic data.[70] Some of the values are given in Table XLI.

Table XLI.—Thermodynamic Functions for NH_4^+(g) *in g.-cal./deg./mole*

Temperature, °K.	$C_p°$	$(H°-H_0°)/T$	$-(F°-H_0°)/T$	$S°$
200	7·98	7·98	33·25	41·23
298·16	8·34	8·04	36·43	44·47
400	9·30	8·23	38·81	47·04
600	11·91	9·03	42·27	51·29
800	14·47	10·08	45·00	55·08
1000	16·65	11·19	47·36	58·55

From the lattice energy of NH_4Cl the heat of formation of NH_4^+(g) is 154 kcal./mole, and for the protonation reaction $NH_3(g)+H^+(g) \rightarrow NH_4^+(g)$ at 298·16°K., the entropy was calculated as $-27·55$ e.u., the heat of reaction as -202 kcal./mole and the free energy of reaction as -194 kcal./mole. Other calculations of the proton affinity of ammonia have given -206 kcal./mole[71] and -214 kcal./mole.[72, 73]

The standard entropy at 298·1°K. of the aqueous ammonium ion is $26·6 \pm 0·5$ e.u.[74]

The partial molal heat capacity of the aqueous ammonium ion at infinite dilution is $-6·6$ g.-cal./degree/g.-ion.[75] The entropy of hydration of NH_4^+ is -11 e.u.[70] and its heat of hydration is 79 kcal./mole.[70, 76]

Ammonium ion activities in aqueous solutions have been measured using cells containing ion-exchange resin membranes.[77–80]

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SECTION VII (a)

THE CHEMICAL PROPERTIES OF AMMONIA

BY J. D. F. MARSH

REACTIONS OF AMMONIA WITH ELEMENTS AND THEIR COMPOUNDS

Reactions with Hydrogen and Deuterium

GASEOUS REACTIONS

Reaction with molecular hydrogen to give the neutral ammonium molecule does not occur at low pressures,[1] but calculations show that at 0°K. a transition should occur from a mixture of crystalline ammonia and hydrogen to metallic ammonium at a pressure between 60,000 and 140,000 atm.[2]

The reaction of hydrogen atoms with ammonia to give NH_2 and H_2 has an activation energy of 8·5 kcal./mol.,[3] and the exchange of deuterium atoms with ammonia has an activation energy of 11 kcal./mol.[4] The α-particle-induced exchange reaction between hydrogen and deuterium is inhibited by ammonia as a result of chain breaking reactions of H and D atoms with ammonia. The interaction involves only van der Waals forces and the rate of exchange between atomic deuterium and ammonia is not appreciable.[5, 6]

From statistical mechanical calculations and experimental determinations, the equilibrium constants given in Table I have been obtained for the following reactions[7]:

$$\begin{array}{lll}
NH_3 + NHD_2 \rightleftharpoons 2NH_2D & & K_1 \\
NH_2D + ND_3 \rightleftharpoons 2NHD_2 & & K_2 \\
NH_3 + HD \rightleftharpoons NH_2D + H_2 & & K_3 \\
NHD_2 + D_2 \rightleftharpoons ND_3 + HD & & K_4 \\
NH_3 + HDO \rightleftharpoons NH_2D + H_2O & & K_5 \\
NHD_2 + D_2O \rightleftharpoons ND_3 + HDO & & K_6
\end{array}$$

Table I.—Equilibrium Constants for Exchange Reactions of Ammonia

Temperature, °C.	K_1	K_2	K_3	K_4	K_5	K_6
0	2·92	2·88	6·85	2·59	1·64	0·732
25	2·94	2·90	5·83	2·23	1·61	0·719
100	2·97	2·94	4·10	1·62	1·56	0·694
300	3·00	2·98	2·53	1·05	1·50	0·661
500	3·00	2·99	2·07	0·87	1·49	0·663
∞	3	3	3/2	2/3	3/2	2/3

K_3 was found to be 1·9 at 300°C.[8, 9] and $0{\cdot}972\, e^{509/T}$ at 210–295°K.[10] The application of the rule of the geometric mean to these equilibria has been discussed.[11–13]

The mercury-photosensitized exchange reaction between deuterium and ammonia has been studied at 30–600°C.[14] and the thermal reaction at 680–780°C.[15]; both reactions proceed by the chain mechanism:

$$\begin{aligned} D_2 &\rightleftharpoons D+D \\ NH_3+D &\rightleftharpoons NH_2D+H \\ H+D_2 &\rightleftharpoons HD+D \end{aligned}$$

CATALYSED REACTIONS

Many metals and oxides catalyse the exchange reaction, platinum being particularly active even at -20°C.[16] The order of decreasing activity of a number of evaporated metal films is Pt, Rh, Pd, Ni, W, Fe, Cu, and Ag.[17] The variation in activity is due to an increase in the activation energy from 5·2 kcal./mol. for Pt to 14·1 kcal./mol. for Ag, the temperature at which the reaction proceeds at a convenient rate increasing from 235°K. for Pt to 544°K. for Ag. The initial product is always NH_2D, the other deutero-compounds forming successively, and the relative concentrations of the deutero-ammonias are the same with all the catalysts. This is because only one hydrogen atom is exchanged at a time.[17]

Other authors have studied the exchange reaction on various platinum catalysts,[18, 19] nickel films[20, 21] and powders,[18, 22] tungsten films,[20] iron films[20] and powders[23, 24] and on selenium coated nickel.[25] On a singly promoted iron catalyst the activation energy is 13 kcal./mol., and the kinetics of the reaction, in particular a decrease in the reaction rate at high ammonia pressures, show that the mechanism involves reaction between adsorbed ammonia molecules and deuterium atoms.[23, 24, 26]

The exchange between NH_3 and ND_3 occurs on iron and rhenium catalysts.[27]

REACTIONS IN SOLUTION

In aqueous solution exchange between NH_4^+ and D_2O is very slow; on the other hand NH_3, with a free electron pair, exchanges practically instantaneously.[28, 29]

Complete exchange occurs on dissolving ammonium chloride containing 14% of ^{15}N in liquid ammonia and rapidly evaporating the ammonia.[30] Exchange between ND_3 and N_2H_4 is also rapid.[31] By continuous fractionation for 630 hours the concentration of ^{15}N was increased to about 5% as a result of the equilibrium:

$$^{15}NH_3\ (\text{gas}) + {}^{14}NH_4^+\ (\text{soln.}) \rightleftharpoons {}^{14}NH_3\ (\text{gas}) + {}^{15}NH_4^+\ (\text{soln.})$$[32]

Direct measurement of the equilibrium constant for this reaction using a mass spectrometer gave a value 50% higher than that calculated from fractionation experiments.[33]

Reactions with Halogens

Gaseous ammonia reacts with fluorine to give a steady flame which is yellow in colour with a greenish tinge. The flame is not always self-igniting and the reaction apparently requires a small activation energy. The flame spectrum contains strong bands due to NH_2 and NH radicals.[34] About 6% of NF_3 has been obtained from the reaction products.[35] Similar flames are obtained with chlorine trifluoride.[36] With aqueous ammonia the products of reaction with fluorine include N_2, O_2, NO_3^-, NO_2^-, N_2H_4 and N_2O.[37]

Gaseous ammonia and chlorine react to give a number of products:

$$\begin{aligned} Cl_2+2NH_3 &\rightarrow NH_2Cl+NH_4Cl \\ 2Cl_2+3NH_3 &\rightarrow NHCl_2+2NH_4Cl \\ 3Cl_2+4NH_3 &\rightarrow NCl_3+3NH_4Cl \\ 3Cl_2+8NH_3 &\rightarrow N_2+6NH_4Cl \end{aligned}$$

Up to 90% of the theoretical yield of chloramine can be obtained at a relatively high $NH_3:Cl_2$ molar ratio, e.g. 20:1,[38] whereas the yield of nitrogen trichloride is high with approximately equimolar mixtures.[39] At very high $NH_3:Cl_2$ ratios hydrazine is formed by the reaction:

$$NH_2Cl + 2NH_3 \rightarrow NH_2{\cdot}NH_2 + NH_4Cl$$

the yield being 30% of the theoretical at a molar ratio of 270:1.[40] The same reactions occur when chlorine is bubbled into liquid ammonia.[40–42] In aqueous solution the products depend on the pH: in hydrochloric acid or acetic acid solution at $pH < 3$ nitrogen trichloride is formed, in phosphate buffers at pH 3–5 $NHCl_2$ is formed and in sodium hydroxide solutions at $pH > 8$ chloramine is the main product.[43] The maximum yield of hydrazine from chlorine and aqueous ammonia is 18%,[44] whereas up to 80% can be produced from chloramine and ammonia in the presence of sodium hydroxide.[45–47]

With excess of chlorine the chloramines are oxidized to nitrogen, nitrous oxide and nitrates.[48–50] In the reaction of sodium hypochlorite or sodium hypobromite with aqueous ammonia or ammonium salts, nitrogen is the main product, e.g.:

$$3NaOCl + 2NH_4OH \rightarrow 3NaCl + 5H_2O + N_2$$

This reaction is not quantitative.[51] With ammonium nitrate and potassium hypobromite, 0·4% of the ammonia is oxidized to nitrate[52] and nitrous oxide is also formed.[53] The amount of nitrous oxide formed is markedly increased by the presence of cupric ions.[54] Oxidation of ammonia containing ^{15}N in the presence of hydrazine or hydroxylamine gives residual hydrazine or hydroxylamine containing no excess of ^{15}N, indicating that these compounds are not intermediates in the formation of nitrogen or nitrous oxide from ammonia.[54] Aqueous ammonia can be oxidized to nitrates and nitrogen by a base exchange material which has taken up manganese ions and has then been oxidized with sodium hypochlorite solution.[55]

Iodine reacts with aqueous ammonia, the first product being iodamine. With excess of iodine nitrogen tri-iodide is precipitated[56]:

$$I_2 + 2NH_3 \rightarrow NH_2I + NH_4I$$
$$NH_2I + 2I_2 + 3NH_3 \rightarrow NH_3{\cdot}NI_3 + 2NH_4I$$

Iodamine[57] and especially nitrogen tri-iodide[56] are unstable, decomposing to give nitrogen by the reactions:

$$4NH_2I \rightarrow 2NH_4I + N_2 + I_2$$
$$2NH_3{\cdot}NI_3 \rightarrow 2NH_3 + N_2 + 3I_2$$

Thus if iodine is shaken with hot aqueous ammonia, nitrogen is evolved and the solution contains ammonium iodide and traces of ammonium iodate.[58] The reaction between ammonia and iodine in carbon tetrachloride solution yields mainly an addition product, xNH_3,yI_2, and small quantities of hydrazine and hydroxylamine are also formed.[59]

For the action of ammonia on the hydrogen halides see the corresponding ammonium salts.

Reactions with Sulphur, and Sulphur, Selenium and Tellurium Compounds

The reaction between aqueous ammonia and sulphur starts at 70–75°C., the products being ammonium sulphide, polysulphide and thiosulphate.[60] A more reactive form of sulphur can be made by dissolving sulphur in sulphur trioxide and treating the disulphur trioxide with pyridine. The sulphur so formed reacts with ammonia to give N_4S_4 and S_7NH.[61]

When ammonia is passed into a petroleum naphtha solution of S_2Cl_2, a mixture of NH_4Cl, N_4S_4 and S is precipitated; if rubber is also present in the solution the precipitate contains in addition compounds of rubber and sulphur.[62] The red diamide of imidodisulphinic acid, $HN(SONH_2)_2$, is obtained on dropping $SOCl_2$ into liquid ammonia. In the gas phase, however, the reaction: $SOCl_2 + 3NH_3 \rightarrow SONH$

$+2NH_4Cl$ occurs with the liberation of much heat.[63] Addition of SO_2Cl_2 in petroleum ether to excess of liquid ammonia yields NH_4Cl, $SO_2(NH_2)_2$ and $NH_4N(SO_2NH_2)_2$.[64]

Trisulphuryl chloride, $S_3O_8Cl_2$, reacts with ammonia, without formation of an amide, by ammonolysis at the S–O–S linkages.[65] Sulphur dioxide and ammonia, in the presence of a trace of water, form a white to yellow-orange waxy solid of composition $NH_2{\cdot}SO_2H$ with excess of SO_2, and form $NH_2{\cdot}SO_2NH_4$ with excess of NH_3 [66]; the same products can be formed from the dry gases.[67, 68] Reaction of ammonia with sulphur dioxide and chlorine yields sulphamide,

$$4NH_3+SO_2+Cl_2 \rightarrow SO_2(NH_2)_2+2NH_4Cl$$ [69]

Sulphur trioxide and ammonia react to give the compounds $(NH_4SO_3)_2N{\cdot}NH_4$, $(NH_4SO_3)_2{\cdot}NH$, $NH_4SO_3{\cdot}NH_2$, $NH_2{\cdot}SO_2{\cdot}NH_2$, $(NH_4)_2SO_4$, and $(NH_4)_2S_3O_{10}$ in proportions which depend on the molar ratio of the reactants, on the temperature and on the presence of water or other solvents[70–81]; $(SO_2NH)_3$, $(SO_2NH)_4$ and $HO{\cdot}SO_2(NHSO_2){\cdot}OH$ can also be formed.[82] With excess of ammonia $(NH_4SO_3)_2$-$N{\cdot}NH_4$ is the major product, whereas if $ClSO_3H$, $ClSO_3Na$ or the addition compounds of sulphur trioxide with pyridine, dimethylaniline or dioxan are treated with excess of ammonia, ammonium sulphamate, $NH_4SO_3NH_2$, is the main product.[83]

Ammonium sulphamate is also formed on adding solid potassium pyrosulphate to cold aqueous ammonia.[84] Addition of the sulphates of hydrazine, methylhydrazine, hydroxylamine and semicarbazide to liquid ammonia gives the corresponding free bases in almost quantitative yield, ammonium sulphate-3 ammoniate being precipitated as it is insoluble in ammonia.[85]

The heat of dissociation of ammonium hydrogen selenide:

$$NH_4HSe\ (s) \rightarrow H_2Se\ (g)+NH_3\ (g)$$

calculated from measurements of the dissociation pressure, is 27·6 kcal./mol.[86] The corresponding value for ammonium hydrogen telluride is 12·28 kcal./mol.[87] Tellurium dichloride reacts with liquid ammonia according to the equation:

$$3TeCl_2+8NH_3 \rightarrow 3Te+6NH_4Cl+N_2$$ [88]

Reactions with Nitrogen, Phosphorus and Arsenic Compounds

The yellow after-glow of active nitrogen is not quenched completely by ammonia. No hydrazine can be detected as a product over the temperature range −5° to 440°C., and it was assumed that the reaction takes place between nitrogen atoms and ammonia to give nitrogen and hydrogen only.[89]

Nitrous oxide does not react with ammonia below 100°C.,[90] but the flame propagation limits extend from 2% to 75% of ammonia.[97] Nitric oxide reacts with ammonia at 100°C. to give nitrogen and traces of ammonium nitrate and ammonium nitrite.[90] The kinetics of the reaction have been studied both in the gas phase[93–94] and on the surface of a platinum filament.[95] Nitrogen dioxide reacts with ammonia at 25–100°C. to give mainly nitrogen, water and ammonium nitrate with traces of nitrous oxide, nitric oxide and ammonium nitrite.[90, 96] The temperature coefficient of the rate of reaction is negative, suggesting that N_2O_4, not NO_2, is the reactive species.[96, 97] Bands characteristic of NH, NH_2 and OH radicals are observed in flames of ammonia and nitrous oxide, nitric oxide, nitrogen dioxide or nitric acid.[98–100]

Nitrous acid reacts with ammonia or the ammonium ion to form nitrogen,[101] and the reaction is catalysed by chloride or bromide ions.[102, 103] Nitryl chloride reacts violently with liquid ammonia at −75°C. to yield chloramine, hydrazine, ammonium nitrite and ammonium chloride. The reaction in the gas phase is not violent and the same products are formed.[104] The reaction of dinitrosyl pyrosulphate with ammonia has been compared with the corresponding reaction of nitrosyl chloride.[105]

Baker found no reaction between dry ammonia and dry phosphorus pentoxide (Mellor, VIII, 220), but more recent work has indicated that rapid reaction occurs.[106–108] When the reactants are not dried the first product is the diammonium salt of amidopyrophosphoric acid and further reaction with ammonia yields the triammonium salt.[109]

On treating phosphorus pentachloride with dry ammonia at −50°C. the white diiminoamide, $P(NH)_2NH_2$, is formed. This decomposes in vacuo at 350–400° to form phospham, PN_2H, and ammonia; at 480° P_3N_5 and ammonia are formed and at 700° phosphorus and nitrogen result.[110, 111] With phosphorus trichloride the initial product is phosphorus amide, $P(NH_2)_3$, which on heating in vacuo gives as decomposition products $PNHNH_2$, $P_2(NH)_3$, P_4N_6 and PN.[112, 113] A polyphosphoryl amide is formed by reaction of anhydrous ammonia with phosphoryl chloride in a hydrocarbon solvent and subsequently heating the mixture to 200°C.[114]

Arsenic selenide reacts with liquid ammonia to form a voluminous yellow precipitate and a yellow-orange solution according to the equation:

$$As_2Se_3 + 4NH_3 \rightarrow NH_4AsSe(NH_2)_2\ (\text{ppt.}) + NH_4AsSe_2\ (\text{soln.})$$

The precipitate loses ammonia at room temperature and forms deep red $AsSeNH_2$.[115]

Reactions with Carbon and Silicon Compounds

CARBON COMPOUNDS

Ammonium carbamate is formed rapidly when carbon dioxide is passed into liquid ammonia.[116] The reaction in the gas phase is influenced by small concentrations of water vapour[117]; no reaction occurs on mixing the gases after intensive drying,[118, 119] although reaction can still occur in the liquid phase.[119] At 20–40°C. the gaseous reaction is of the third order.[120] The rate of reaction in aqueous solution has been calculated from the observed temperature gradient when the reactants flow along a tube,[121] and the theoretical treatment of the kinetics of simultaneous absorption and chemical reaction has been applied to absorption of carbon dioxide by aqueous ammonia.[122, 123] When liquid ammonia and carbon dioxide are heated under pressure to 150–250°C., urea is formed in yields of 35–40%.[124–127] The equilibria involved in the formation of urea have been studied[128–132] and the kinetics of the reaction investigated.[133] In the presence of alumina and thoria catalysts at above 400°C., ammonium thiocyanate is the chief product but some urea is also formed.[134] At −35 to 0°C. urea reacts with ammonia to form the ammoniate, $CO(NH_2)_2,NH_3$.[135] At 300°C. under pressure in the presence of ammonium nitrate 29% of guanidine is formed.[136] A yield of 65% of guanidine carbonate is obtained from ammonia, carbon dioxide and calcium cyanamide at 150°C.[137]

At low temperatures and pressures in the presence of organic solvents the main reactions between ammonia and carbon disulphide are[138, 139]:

$$2CS_2 + 4NH_3 \rightarrow NH_4CS_2NH_2 + NH_4CNS + H_2S$$

and

$$2CS_2 + 4NH_3 \rightarrow (NH_4)_2CS_3 + NH_4CNS$$

In aqueous solution ammonium trithiocarbonate is formed.[140] At 110°C. in an autoclave ammonia and carbon disulphide react to form ammonium thiocyanate and ammonium tri-thiocarbonate.[141, 142] At 150–190°C., 10–22% of thiourea is formed,[143] at 250°C. 18% of guanidine is formed,[144] and at 300°C. 10% of melamine is produced.[145] Guanidine thiocyanate can be made continuously by passing ammonia and carbon disulphide into molten guanidine thiocyanate at 170–300°C.[146]

Carbonyl sulphide and ammonia react together according to the equation:

$$COS + 2NH_3 \rightleftharpoons NH_4S(CO)NH_2 \rightarrow CO(NH_2)_2 + H_2S$$

When the reactants are mixed in the gas phase at 0–50°C. in glass apparatus the reaction takes place on the walls.[147] Above 40°C. ammonium thiocarbamate decomposes to urea, and the equilibrium yield of urea is higher from carbonyl sulphide than from carbon dioxide and ammonia.[148–150]

Carbon monoxide and ammonia react in an autoclave at 120–130 kg./sq. cm. and 90°C. in the presence of various catalysts to give formamide, the highest yield being 95% in presence of sodium glycerate.[151] Chromium oxide catalyses the reaction at atmospheric pressure,[152] and formamide is the primary product of the photochemical reaction of ammonia with carbon monoxide.[153] Hydrogen cyanide is formed when a mixture of ammonia and carbon monoxide is passed over various catalysts at 400–550°C. (Mellor, VIII, 221). The catalysts examined include thoria, zirconia, alumina, ceria, vanadium trioxide and uranium dioxide,[154, 155] iron carbide and molybdenum,[156] manganese dioxide,[157] and an alumina-supported sulphuric acid catalyst promoted by thoria.[158–160] Hydrogen cyanide is also formed by the action of ammonia on hydrocarbons at 800–1200°C. in the presence of catalysts[155, 161, 162]; air or oxygen may also be added to make the reaction exothermic,[163–170] e.g.:

$$2NH_3 + 2CH_4 + 3O_2 \rightarrow 2HCN + 6H_2O + 229{,}800 \text{ g.-cal.}$$

Hydrogen cyanide is also formed from ammonia and methane or acetylene under the action of a high frequency arc discharge.[171, 172]

Phosgene reacts with ammonia to form urea, melanuric acid and cyanuric acid.[173, 174] Carbon tetraiodide is reversibly ammoniated in boiling liquid ammonia to form $CI_4,2NH_3$.[175] The rate constants at 10°C. for the reaction of aqueous ammonia with cyanogen bromide and cyanogen iodide are 0·195 and 0·000456 respectively.[176]

SILICON COMPOUNDS

Silicon tetrachloride reacts with ammonia at room temperature to form ammonium chloride and $Si(NH)_2$.[177, 178] Silicon tetrafluoride forms a stable white solid with ammonia.[179] Silicon tetrabromide reacts with 4–6 moles of ammonia according to the conditions of temperature and concentration.[180] The reaction of ammonia with silicon dibromide results in replacement of bromine atoms by NH_2 groups, condensation of NH_2 groups to NH bridges and cleavage of Si–Si bonds.[181] Gaseous silicon monoxide reacts with ammonia to form a polymeric silicon oxy-imide, $(SiONH)_x$.[182]

Ammonia reacts with germanium tetrachloride to form germanium imide, $Ge(NH)_2$,[183] and the same product is obtained from germanium tetraiodide[184]; GeH_3Cl with ammonia forms NH_4Cl, GeH_4 and $(GeH)_x$; GeH_2Cl_2 forms Ge and NH_4Cl.[185]

Reactions with Boron Compounds

Boron hydrides form ammoniates with ammonia, e.g. $B_2H_6,2NH_3$, $B_4H_{10},4NH_3$, $B_5H_9,4NH_3$.[186–188] $B_2H_6,2NH_3$ exchanges its hydrogen atoms attached to nitrogen with NH_3 at $-78°$ to $+18°$C., but not the hydrogen atoms attached to boron.[189] On heating above 100°C. $BH_2 \cdot NH_2$ is formed.[190] Ammoniates are also formed by the methyldiboranes.[191]

Boron trifluoride forms the stable addition compound BF_3,NH_3.[192] The proton magnetic resonance spectrum of a liquid ammonia solution of boron trifluoride shows a chemical shift to lower field strength.[193] The rate of reaction of ammonia and boron trifluoride in spherical diffusion flames has been calculated from the temperature distribution.[194, 195] Ammonia reacts with boron tribromide according to the equation:

$$2BBr_3 + 9NH_3 \rightarrow B_2(NH)_3 + 6NH_4Br$$ [180]

A similar reaction occurs with boron tri-iodide.[196] Chromium, iron and tungsten borides react with ammonia at different temperatures to form the metal nitride and boron nitride.[197]

Reactions with Metal Salts

Many metal salts combine with ammonia to form stable ammoniates. Vapour pressure measurements have been reported for various cupric salts,[198] magnesium nitrate,[199, 200] magnesium chloride,[201] zinc chloride,[202] calcium chloride,[203, 204] barium chloride,[204, 206] ferrous chloride, nickel chloride and manganese chloride.[207] The kinetics of the reactions between ammonia and silver chloride,[208, 209] zinc chloride[210] and cadmium chloride[211] have been studied.

Gaseous ammonia reacts with mercuric chloride and bromide at room temperature to form the ammoniates $HgCl_2,2NH_3$ and $HgBr_2,2NH_3$.[212] With concentrated aqueous ammonia the following reactions also occur[213]:

$$HgCl_2,2NH_3 \rightleftharpoons Hg,NH_2Cl+NH_4Cl$$
$$2Hg,NH_2Cl \rightleftharpoons Hg_2NCl+NH_4Cl$$

Similar reactions occur with $HgBr_2,2NH_3$ and $HgI_2,2NH_3$.[213, 214] Dilute ammonia precipitates $3HgO,HgCl_2,2NH_3$ from a solution of mercuric chloride,[215] and a similar precipitate of less definite composition is obtained from aqueous mercuric bromide.[216] The formation of Hg_2NH_2Cl by the action of ammonia on mercurous chloride has been reported,[217–219] but some authors maintain that decomposition to form mercury and mercuric compounds always takes place.[220–225] Thus, with gaseous ammonia, mercury and $HgCl_2,2NH_3$ are formed, with liquid ammonia some $HgNH_2Cl$ is also formed, and with aqueous ammonia Hg_2NCl,H_2O is a major product.[226] The canary-yellow precipitate obtained by the reaction of mercuric salts, ammonia and alkali thiocyanates has the composition Hg_2ONH_2SCN.[227]

Titanium tetrachloride reacts with liquid ammonia to form $TiCl_4,8NH_3$, but with gaseous ammonia at −36° to −63°C. amidochlorides, e.g. $Ti(NH_2)_3Cl$, are formed.[228] Zirconium tetrachloride forms $ZrNH_2Cl_3$ as well as $ZrCl_4,8NH_3$, whereas thorium tetrachloride forms ammoniates only.[229] Similarly zirconium tetrabromide ammonates in liquid ammonia at low temperatures but ammonolyses at higher temperatures.[230] Amidochlorides are also formed with niobium pentachloride[231] and tantalum pentachloride.[232] The formation of metal ammines in aqueous solution was treated by Bjerrum as a statistical problem involving the formation of all intermediate steps, and stability constants were measured for the complexes of lithium, silver, thallous, calcium, magnesium, zinc, cadmium, mercuric, cobaltous, nickel and cobaltic ions.[233] However, data for the formation of ammines by silver, mercury, zinc, nickel and cobalt have been interpreted by simpler reactions.[234]

The precipitation of magnesium hydroxide from magnesium sulphate or chloride solutions by ammonia does not follow the mass-action law.[235] Extensive adsorption of divalent cobalt, nickel, manganese, copper, zinc and cadmium ions occurs during the precipitation of trivalent iron, aluminium and chromium hydroxides by ammonia.[236, 237] The lowest temperatures for reduction of the alkali metal sulphates in a stream of ammonia are 720°C. for lithium, 770°C. for sodium, 800°C. for potassium, 790°C. for rubidium and 770°C. for cæsium sulphates.[238]

Calcium carbonate reacts with ammonia at 750–800°C. to form calcium cyanamide[239, 240]; barium and strontium carbonates react at 800–900° to form the corresponding cyanamides.[239] The equilibrium constants of these three reactions have been measured.[241] Magnesium, zinc and lead carbonates cannot be converted to their cyanamides, but are reduced to the metals.[239]

Uranium nitrate is formed by reaction of ammonia and uranium hydride.[242] The photochemical reaction between iron carbonyl and ammonia in the gas phase yields urea and other products and is catalysed by silica gel.[243]

Ammonia as an Accelerator or Inhibitor

In the presence of ammonia photochemical reactions between oxygen and hydrogen or carbon monoxide occur at 120–420°C. The chain reactions are initiated by hydrogen atoms formed by decomposition of the ammonia.[244, 245] The polymerization of ethylene is also photosensitized by ammonia at 100°C.[246] At 500°C. ammonia sensitizes the thermal hydrogen–oxygen reaction,[247] as a result of the formation of nitric oxide.[248] Ammonia activates oxidation reactions by hypochlorite ions in aqueous solution.[249]

Ammonia accelerates the reaction between powdered calcium oxide and liquid hydrogen cyanide,[250] the decomposition of sodium amalgam,[257] the decomposition of calcium carbonate,[252, 253] and magnesite,[253, 254] the dehydration of gypsum and chromia gel,[255] the ageing of clay cracking catalysts,[256] and the rate of formation of amorphous sulphur.[257] Traces of ammonia facilitate track formation in a continuous cloud chamber[258] and increase the number of ice crystals formed by silver iodide in a supercooled cloud.[259] The presence of ammonia increases the separation of H_2O and D_2O during electrolysis of aqueous potassium hydroxide containing D_2O.[260] The copper–ammonia complex catalyses the decomposition of hydrogen peroxide.[261] The activity of wood charcoal for the decomposition of hydrogen peroxide is increased by heating in ammonia gas.[262]

The presence of ammonia during the preparation of a nickel catalyst increases subsequent yields in the synthesis of hydrocarbons from carbon monoxide and hydrogen, but addition of ammonia during the reduction lowers the yields.[263] The presence of ammonia during the synthesis increases the yield of liquid hydrocarbons over iron catalysts,[264] but decreases the yield over a cobalt catalyst.[265]

The addition of ammonia narrows the explosive limits of hydrogen–air[266, 267] and carbon disulphide–air[268] mixtures. The chlorine-sensitized photochemical formation of phosgene from chloroform, chlorine and oxygen,[269] and the acetone photosensitized decomposition of carbon tetrachloride[270] are both inhibited by small amounts of ammonia. Pure dry ammonia poisons liquid-phase hydrogenation reactions on nickel or platinum catalysts,[271] and the presence of ammonia inhibits the removal of nitric oxide from town gas by ferrous sulphide.[272] The ammonium ion is an inhibitor for the urease catalysed hydrolysis of urea.[273]

Ammonia has little influence on the slow oxidation of *cyclo*hexane by a silent electric discharge[274] or on the oxidation of sulphur dioxide over a vanadium catalyst.[275] The supposed ammonia-induced decomposition of nitric oxide[276] was later shown to be due to a flaw in the experimental technique.[277]

Reactions in Liquid Ammonia

Ammonia is an ionizing solvent comparable with water, and there are many analogies between reactions in liquid ammonia and in water (Mellor, VIII, 276). According to Kraus[278] the differences between the chemistry of solutions in liquid ammonia and water are mainly due to the greater inertness of the H–N bond as against that of the H–O bond. In water salts of the weaker acids and bases are largely hydrolysed, and reducing agents stronger than hydrogen react with water with evolution of hydrogen. The chemistry of liquid ammonia solutions is characterized by the availability of reagents of high reducing power and by stable solutions of salts of exceedingly weak acids. Only weak oxidizing agents, such as alkali-metal permanganates and chromates, are available, but solutions of the alkali and alkaline earth metals in liquid ammonia are the strongest homogeneous reducing agents known and react with many elements, salts, hydrides, halides, etc. Sodium in liquid ammonia reacts with the carbonyls of iron and cobalt to yield the carbonyl metallate.[279] A number of authors have reviewed reactions in liquid ammonia[280–286] and the reactions of solutions of the alkali metals.[287–289] Ammonolysis reactions of hydrides, oxides, halides, sulphides and some salts have been summarized, the data for halides being particularly extensive.[290] The polarograph[291] and ion exchange techniques[292] can be used in liquid ammonia, but the glass electrode does not function.[293] In the electrolysis of liquid ammonia, Ohm's law is not obeyed and black deposits are formed on the cathode.[294] With liquid ammonia solutions the loss in weight of various metallic anodes is greater than is to be expected from Faraday's

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law,[295] sometimes because of the formation of ions of unfamiliar lower oxidation states.[296]

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SECTION VII (b)

THE CHEMICAL PROPERTIES OF AMMONIA
(continued)

BY J. D. F. MARSH

DECOMPOSITION OF AMMONIA

Photochemical Decomposition

Considerable interest has been shown in the mechanism of the photochemical decomposition of ammonia, particularly during the period 1930 to 1940. A report[1] published in 1930 reviewed the knowledge of photochemistry at that time, including that of ammonia decomposition.

The quantum yield in the gas phase was studied, using a mercury vapour lamp emitting light up to a wave-length of 1850 A. The yield decreased with decreasing light intensity below total pressures of 300 mm. Hg, but at higher pressures was practically independent of pressure, but decreased with protracted illumination.[2] Other workers[3] found the variation of quantum yield with light intensity to be in accord with a rate equation derived from the mechanism suggested by Mund and van Tiggelen.[4, 5] Between 2026 and 2138 A. the quantum yield was independent of the 'purity' of the light, but dependent on pressure, with a maximum between 65 and 120 mm. Hg.[6] At pressures between 1 and 8 atm. and wave-lengths 2099 to 2194 A. the photochemical decomposition of ammonia appeared to be independent both of the wave-length of the irradiating light and of the pressure, and had a quantum efficiency of 0·14 at 20°, increasing fourfold at 400°.[7] The quantum efficiency depended on the size of the reaction cell, and the reaction was heterogeneous at ammonia pressures less than 300 mm. Hg,[8] though the mechanism suggested was criticized because rate equations deduced therefrom were found not to fit experimental results.[9] The products of decomposition by the radiation from zinc, aluminium and cadmium sparks were hydrogen and nitrogen in the ratio of 3:1 by volume, the quantum yields being 0·25 at 25° and 0·5 at 500°.[10] The products of decomposition at wave-length 1990 A. and pressures of 2 to 128 mm. Hg are mainly hydrogen and hydrazine, the latter being adsorbed on the walls of the reaction vessel. Under these conditions the quantum yield approaches unity, but under similar conditions of pressure and wave-length the quantum yield for the mercury-sensitized decomposition is only 0·12.[11] This low value may be due to recombination of hydrogen atoms and amino radicals.[12] Many papers discuss both the reaction mechanism[13–20] (though that for the mercury-sensitized reaction was held to be obscure[21]), and the light thrown on the problem by the study of deuteroammonia.[22–25] The step $NH_2+H_2 \rightarrow NH_3+H$ was confirmed[2, 15, 19] and leads to the low quantum yield in the direct photochemical decomposition, as in the mercury-sensitized reaction. It was maintained, however, that a scheme of secondary reactions which excluded the recombination $NH_2+H \rightarrow NH_3$ gives values for the effect of inhibition by hydrogen that are in better agreement with experimental results.[18] One proposed reaction mechanism is[14]:

$$\begin{aligned}&NH_3+h\nu \rightarrow NH_2+H\\&NH_3+H+M \rightarrow NH_4+M\\&NH_4+M \rightarrow NH_3+H+M\\&NH_4+NH_2 \rightarrow \text{either } 2NH_3 \text{ or } NH_3+NH+H_2\end{aligned}$$

H, NH_2 and NH_4 diffuse to the wall
$2NH \rightarrow N_2 + H_2$

Another worker[15] held that the only secondary reactions are:

$$H + H \rightarrow H_2$$
$$NH_2 + NH_2 \rightarrow 2H_2 + N_2$$
$$H + NH_2 \rightarrow NH_3$$

The products from ammonia, as from aliphatic primary and secondary amines, arise mainly from the rupture of the N–H bond.[16] Hydrazine is produced both by the photochemical and by the glow discharge decomposition of ammonia.[26] In the absorption spectrum of decomposed ammonia the NH band could not be detected.[20] The kinetics of the decomposition of ammonia and deuteroammonia have been examined and an expression has been deduced giving values for the quenching ratio and the decomposition probability after quenching.[27]

Less work has been done on flowing systems. In a fast-flowing system the rate of production of hydrazine is reduced to one-third by presaturation with mercury vapour,[28] and the quantum yield is twice that for static conditions at the same pressure.[29]

The photochemical decomposition in the presence of other substances has also been studied. The presence of inert gas does not alter the quantum yield, but hydrogen causes a sharp decrease.[2] Various products including hydrogen, nitrogen, *iso*propylamine, propylene and 2,3-dimethylbutane were identified as resulting from the photochemical decomposition of ammonia in the presence of propane and oxygen,[30] while in the presence of ethylene or ethylene–hydrogen mixtures a liquid polymer of ethylene was produced.[31] The interaction of nitric oxide with the radicals $\text{-}NH_2$ and $\text{-}N_2H_3$ (produced during the photolysis of ammonia and hydrazine respectively) showed that the total nitrogen content appeared as free nitrogen in the former case but as a mixture of nitrogen, ammonia and nitric oxide in the latter.[17] Some work has been carried out on the photochemical decomposition of ammonia adsorbed on alumina, iron, nickel and copper[32] and on copper sulphate and magnesium oxide.[33]

Decomposition by Electric Discharge

The decomposition of ammonia by glow discharge has been extensively studied. The ionization efficiency was found to fall between that of hydrogen and nitrogen for electron energies of 475 to 900 ev. in the negative glow[34] at pressures up to 9 mm. Hg, while the electron energy in the positive column was 10–30 ev. under similar conditions.[35] At 6 mm. Hg pressure the generation of ions in the positive column was found to be 3×10^{15} ions per sec. per unit length of tube, while the decomposition of ammonia molecules was found to be 5×10^{16} molecules per sec. per unit length of tube.[36] The conclusion that the decomposition is not wholly attributable to ionization was confirmed by Ouchi and Takamatsu,[37] one of whom proposed the mechanism[38]:

$$NH_3 + e \rightarrow NH_3^* + e$$
$$NH_3^* \rightarrow NH + H_2$$
$$NH + NH_3 \rightarrow N_2 + 2H_2$$

Evidence for the validity of this mechanism is the detection of the -NH radical in the emission spectra when ammonia flows through a discharge tube.[39] In the arc discharge NH_2 radicals have been identified.[40] A method has been described for measuring the rate of decomposition of ammonia at the instant when the discharge begins; this rate, highest at the centre of the positive column, is found to increase with increase of current.[41] The yield of hydrazine, formed in the positive column near its boundary with the Faraday dark space,[42, 43] was found to increase as (electric power × residence time in glow) decreased.[43–46]

According to one worker, changing the flow rate of the ammonia did not have any considerable effect on the hydrazine yield,[47] but this was affected by back reaction involving atomic hydrogen and the yield thus increased, by the catalysis of atomic hydrogen removal, when the walls of the vessel were coated with platinum black.[48] At 4–6 mm. Hg pressure, 50 and 500 cycle/sec. currents at 4300 and 6400 volts converted 0·09 to 0·27% of the ammonia to hydrazine, 5·8% of the total electrical energy being thus utilized.[49] The decomposition of ammonia by glow discharge is dependent on temperature[50] and current, but independent of pressure. The ions N_2^+, O_2^+, He^+, A^+, Hg^+ and NH_3^+ catalyse the decomposition, but H_2^+ ions have no effect.[51]

Reaction of ammonia with ethylene in the glow discharge was found to produce cyanides, that with oxygen giving nitrides. The glow is extinguished immediately by copper, while iron oxide, tin, nickel, iron and platinum give an induction period, molybdenum and tungsten having no effect.[52] The decomposition of ammonia by a silent discharge is initially of the first order,[53] but the subsequent progress of the decomposition is retarded by the products.[53–56] Some studies have been made of starting voltages and of current–voltage characteristics in various gases including ammonia[57–59] and of the power consumption under various conditions as indicated by a calorimetric technique.[60] Under silent discharge conditions the formation of hydrazine may be dependent on pressure[55, 61] and patents exist whereby ammonia is condensed to hydrazine using a composite electric discharge and tungsten or copper–lithium electrodes.[62, 63] In a high frequency discharge ammonia is adsorbed more easily than hydrogen on the walls of the tube, but the adsorption, reversible for hydrogen, is irreversible for ammonia. Once the walls are saturated with ammonia, the residual gas decomposes into hydrogen and nitrogen.[64] The amount of ammonia formed by the interaction of active nitrogen and hydrogen atoms is said to be proportional to the concentration of hydrogen atoms provided the nitrogen atoms are present in excess.[65] When ammonia is subjected to an electrodeless discharge in a glass tube surrounded by a copper solenoid attached to a Tesla coil, it dissociates to the extent of 67%. A 30% yield of ammonia is obtained if the starting materials are hydrogen and nitrogen.[66]

Studies have been reported of the decomposition of ammonia by atomic ion impact,[67] by α-rays[68–70] and by electron impact.[77, 72] When mixtures of hydrogen, nitrogen and ammonia in a stoicheiometric mixture are irradiated at 24° with radon, the equilibrium concentration of ammonia is 4·7%.[73]

Decomposition on Iron

Considerable attention has been given to the decomposition of ammonia on iron and alkali-promoted iron catalysts. Values for the activation energy found are 12·4 kcal./mol. at 300–350°, 39·7 kcal./mol. above 350°,[74] 11·7 kcal./mol. between 360° and 375°,[75] 51–54 kcal./mol. at 500–700°[76] and 20 to 50 kcal./mol. at 475–750°.[77] It has been claimed that the reaction is of zero order,[78] or is a complex reaction of first order followed by one of fractional or zero order,[79, 80] or is a first order reaction which is pseudo-zero order because of certain opposing effects.[81] There is an initial retardation due to the formation of a layer of iron nitride over the active surface.[82] The mechanism of the formation and decomposition of the nitride layer and its effect on the main reaction has been the subject of many studies,[83–89] including one of practical application to the carbonitriding process for case hardening.[90] It has been said that the most active catalyst for ammonia decomposition is that in which 30% of the catalyst surface is covered by the alkali promoter.[91] Considerable differences were noted between pure iron catalysts and iron catalysts promoted with potassium and aluminium oxide, particularly in respect of dependence on temperature and on partial pressures of hydrogen and ammonia.[92] Another worker found that the results are similar for iron and alkali-promoted iron catalysts, but that the reactions are represented by different kinetic equations.[93]

The activities of various forms of iron for the decomposition of ammonia have been compared.[94, 95] The rate-controlling step for the reaction is said to be the desorption of nitrogen from the catalyst surface,[96] the decomposition of iron nitride into nitrogen and iron,[88] or the decomposition of adsorbed ammonia.[91] Adsorption data for nitrogen on iron catalysts have been reported.[98] The effect of gas-film resistance is not observed below 485° [99] and a sharp decrease in activity is noted at the temperature at which a high temperature form of the catalyst is created.[100] The magnetic properties of iron and iron–nickel catalysts for ammonia decomposition have been studied[101, 102] and the lack of effect of external magnetic fields noted and explained.[103]

Decomposition on other Surfaces

Kinetic theory for the decomposition of ammonia on various surfaces has been discussed[104–106] and it is concluded that the reaction mechanism is similar on various catalysts.[107] A review[108] included results on nitrogen deposition on metal surfaces and a comparison of reaction and diffusion rates in carburizing and nitriding processes. The velocity of decomposition of ammonia on quartz has been measured.[109] Much work has been done on the decomposition by platinum catalysts[110–118] and some work on osmium, rhodium and rhenium.[119–121] The decomposition on molybdenum and on tungsten of both NH_3 and ND_3 has attracted a great deal of attention[117, 122–131] and the phenomena of 'ageing' and embrittlement of wires have been considered.[132, 133] Copper, nickel and germanium are other metal surfaces which have been studied.[118, 134–138]

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OXIDATION OF AMMONIA

Ammonia and oxygen react slowly in the temperature range 400–700°C. In a flow system the fraction burned increases rapidly as the ammonia concentration is decreased.[1] Measurements in a static system show that the kinetics of the reaction change sharply at the equimolar mixture. For ammonia-rich mixtures rates are roughly proportional to the product of ammonia and oxygen concentrations, whereas for ammonia-lean mixtures the square of the oxygen concentration is involved. There is a sharp change in rate as the ammonia : oxygen ratio is decreased.[2] The energy of activation is 45 kcal./mol.[2, 3] or 49·5 kcal./mol.[4] Hydrogen is one of the reaction products, particularly at low oxygen partial pressures.[5] The rate of the reaction is reduced by coating the reaction vessel with potassium chloride.[1, 6]

Explosive Limits

Many measurements of the explosive limits of ammonia with air or oxygen have been made (Mellor, VIII, 208). The results depend not only on temperature and pressure, but also on the size of chamber, the means of ignition, the point at which ignition occurs, etc.[7] Some results for the range of explosive percentage by volume in dry air at atmospheric temperature and pressure are: 16·0–27·0%,[8] 16·5–26·8%,[9] 15·0–25·0%[10] and 17·16-25·4% in an open tube compared with 16·09–26·64% in a closed tube.[11] The presence of water vapour has been said to have no effect,[10] to widen the limits,[12] or to suppress the explosion.[9] The explosion limits for mixtures of ammonia with oxygen are 25–75%,[13, 14] and the maximum rate of propagation of the wave-front is 2982 m. per sec. with a mixture containing 75% of ammonia.[14] An increase in pressure up to 20 atm. widens the explosion limits with oxygen[15] or air.[16] The ternary systems ammonia–oxygen–nitrogen[17, 18] and ammonia–oxygen–argon[18] have been studied. A distinction has been drawn between the limits of explosivity and the limits of inflammability[19] and a theory of the inflammability limits has been developed.[20]

The ignition temperatures of ammonia–air mixtures containing 9–57% of ammonia are in the region of 920–1000°C. The same results are obtained with dry and moist air, but addition of hydrogen lowers the ignition temperature considerably.[21] With ammonia–oxygen mixtures the ignition takes place at about 700°C.[22, 23] although higher temperatures are required at reduced pressures.[24] Spark ignition of ammonia–air mixtures has been studied.[25, 26]

Ammonia–Oxygen Flames

The maximum flame propagation velocity of ammonia–oxygen mixtures is 113 cm./sec. at 54% of ammonia, whereas with ammonia–nitrous oxide mixtures the maximum velocity is 73 cm./sec. with 38% of ammonia.[27] On the assumption that the combustion reaction involves chain branching, which is initiated thermally, the activation energy of the chain branching reaction can be calculated as 59 kcal./mol. for ammonia–oxygen flames,[28, 29] and it is even higher for ammonia–nitrous oxide.[30] The maximum flame speed of ammonia–oxygen mixtures increases from 120 cm./sec. to 170 cm./sec. on increasing the temperature of the mixture from 25°C. to 150°C.[31] Stable ammonia–air flames cannot be produced with the gases at room temperature,[27, 32] but with 19·4% of ammonia in air preheated to 150°C. a flame temperature of 1600°C. is obtained. The burning velocity is 21·3 cm./sec. and the products of combustion contain 0·2% of nitric oxide and traces of ammonia. The burning velocity is higher with excess of air than with excess of ammonia, suggesting that self-decomposition of the ammonia occurs and that hydroxyl radicals are especially important for flame propagation.[33 34]

Spectroscopic examination of flat ammonia–oxygen diffusion flames shows bands due to NH_3, NH_2, NH, OH and O_2 on moving from the ammonia to the oxygen side of the flame, the maximum flame temperature being about 2,400°C.[35] The flame consists of two parts, firstly a region of thermal breakdown of ammonia to nitrogen and hydrogen, and secondly a high temperature region where the hydrogen burns in oxygen with nitrogen as a diluent.[36] With premixed flames the maximum concentration of NH radicals is found with 51·5–55·5% of ammonia, at which composition the flame speed is also greatest.[37] Spectrum line reversal measurements show high electronic excitation.[38] Bands due to NH radicals are observed also in spark-induced explosions of ammonia–oxygen mixtures,[39] and measurements of the increase in pressure indicate that the mechanism of these explosions is similar to that at the lower limit of self-inflammation.[40]

Oxygen atoms, produced in a silent electric discharge at a pressure of about 1 mm. Hg, react with ammonia at temperatures down to -183°C. About 1 in 10^5 collisions leads to reaction, the products being water, nitrogen, nitric acid and a yellow precipitate of unknown composition which explodes easily.[41–44]

Liquid ammonia reacts with liquid oxygen at temperatures near the critical temperature to form ammonium nitrate, ammonium nitrite and nitrogen, and a heavy liquid phase separates.[45] Combustion of liquid ammonia with liquid oxygen in a rocket motor gives a temperature of 2790°C. and a characteristic exhaust velocity of 5800 ft./sec.[46] Liquid nitric acid burns in gaseous ammonia.[47]

Oxidation of Ammonia Solutions

Gaseous ammonia reacts with oxygen when irradiated by zinc spark radiation of wave-length 2080 A. at room temperature. The quantum yield is 0·4–0·9 and the reaction products are water, nitrogen, ammonium nitrate and small quantities of ammonium nitrite and hydrogen.[48] Dilute aqueous ammonia is oxidized to ammonium nitrite at room temperature on irradiation with *X*-rays provided oxygen is present.[49] The photochemical oxidation of aqueous ammonia by radiation from a mercury arc proceeds faster the lower the temperature; the main product is ammonium nitrate.[50] The reaction is sensitized by the presence of various solids including zinc oxide,[50] titania,[50–52] thallous chloride,[53] stannic oxide,[54] manganese dioxide[55] and vanadium pentoxide.[55] Ammonium nitrite is the major product of the photo-sensitized reaction.[51, 54] The photochemical oxidation of ammonia is more rapid in sea water than in distilled water.[56] Ammonia is oxidized in the soil[57] and in the presence of litter or humus.[58]

Ammonia can be oxidized electrolytically using a platinum black anode.[59] With an iron anode in a two compartment cell (the anolyte being 16% ammonium carbonate solution with 1% cupric hydroxide as catalyst and the catholyte being 10% potassium hydroxide solution) about 75% of the ammonia is oxidized to ammonium nitrate.[60] The oxidation of ammonia can be used to operate a fuel cell.[67]

Ammoniacal solutions of copper sulphate are not oxidized by air, whereas in ammoniacal solutions of cupric hydroxide ammonia is oxidized by air to ammonium nitrite.[62] Cobalt is also a catalyst for the oxidation of aqueous ammonia.[63] When an ammoniacal solution of potassium ferricyanide is mixed with aqueous silver nitrate, silver ferrocyanide begins to separate in 5–6 hours. The trivalent iron is reduced by ammonia which is oxidized to nitrogen and oxides of nitrogen. Similar reactions occur more slowly with cadmium and zinc sulphates.[64] A loss of ammonia by oxidation to nitrogen can occur in the Kjeldahl method for the determination of nitrogen.[65]

The oxidation of aqueous ammonia to nitrogen by persulphate, catalysed by silver ions, is stoicheiometric only over a very limited range of concentrations.[66, 67] Hydrogen peroxide and ammonia interact slowly in the dark[68]; irradiation with ultra-violet light causes oxidation of the ammonia with a quantum efficiency of 0·16–0·22.[69] Ozonized oxygen containing 5% of ozone produces high yields of

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ammonium nitrate on reaction with aqueous ammonia. Thus at 25°C. in two hours the conversion of ammonia varied from 24·4% to 3·6% with solutions containing from 0·55% to 5·6% of ammonia.[70] The reaction is catalysed by copper, cobalt and nickel ions.[71] A coloured compound is formed in the reaction of ozone with moist liquid ammonia at -75°C.[72]

Oxidation of Gaseous Ammonia on Platinum Catalysts

This reaction has attracted a great deal of attention because of its importance in the manufacture of nitric acid (Mellor, VIII, 209–15). The main reactions which occur when a mixture of ammonia and air is passed over a platinum gauze catalyst are highly exothermic:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O + 217 \text{ kcal.}$$
$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O + 303 \text{ kcal.}$$

If the temperature of the reactants is slowly increased the rate of reaction increases rapidly at about 250°C., there being a discontinuous increase in catalyst temperature (ignition) with a great increase in the conversion.[73, 74] With the gauze temperature at 800–900°C. the rate of reaction is determined by the rate of diffusion of ammonia to the surface of the catalyst.[75, 76] Under these conditions at about atmospheric pressure nitric oxide is the major product with excess of air whilst nitrogen is the major product with excess of ammonia. Nitrous oxide is formed in considerable quantities at lower temperatures only, e.g. at 350–450°.[77–79]

BODENSTEIN'S MECHANISM

Bodenstein originally proposed that the primary reaction was the formation of nitroxyl (Mellor, VIII, 211)

$$NH_3 + O_2 \rightarrow HNO + H_2O$$

and this mechanism is supported by Andrussow.[80] But, as a result of work at 0·01 mm. Hg pressure and 1050–1260°, which gave hydroxylamine, nitrous acid and nitrogen as the major products,[81] Bodenstein developed a mechanism in which hydroxylamine is the primary product[82–84]:

$$NH_3 + O \text{ (ads.)} \rightarrow NH_2OH$$

Formation of NO: $NH_2OH + O_2 \rightarrow HNO_2 + H_2O$
$HNO_2 + O_2 \rightarrow HNO_4$
$HNO_4 \rightarrow NO + O_2 + OH$
Formation of N_2O: $NH_2OH + O \rightarrow HNO + H_2O$
$2HNO \rightarrow H_2O + NO_2$
Formation of N_2: $HNO_2 + NH_3 \rightarrow 2H_2O + N_2$ (at higher temperatures)
$HNO + NH_2OH \rightarrow 2H_2O + N_2$ (at lower temperatures)

By passing mixtures of hydroxylamine and ammonia over the catalyst it was shown that the reaction:

$$NH_2OH + NH_3 \rightarrow N_2 + H_2O + 2H_2$$

does not take place.[84] Wendlandt[85] supported the hydroxylamine mechanism with the exception that nitric oxide formation occurs by the process:

$$4HNO_2 \rightarrow 4NO + 2H_2O + O_2$$

without the intermediate formation of peroxynitric acid. Krauss studied the reaction of oxygen and ammonia on platinum and platinum–rhodium catalysts in a flow system at 10^{-2} mm. Hg and temperatures from 740–1250°C.; he concluded that hydroxylamine is the primary product and that the further oxidation to nitrous acid occurs partly in the gas phase.[86–88] Experiments in a static system at similar temperatures and pressures gave nitric oxide as the main product and no hydroxylamine was observed.[89] The rate is proportional to the ammonia pressure and independent of the oxygen pressure. Thus the oxidation occurs through collision of molecular ammonia with a platinum surface almost completely covered with adsorbed oxygen; at 820°C. and at low pressure the calculated collision rate is twenty times the observed rate of reaction.

RASCHIG'S MECHANISM

As an alternative to the hydroxylamine mechanism some authors prefer the imide mechanism first proposed by Raschig (Mellor, VIII, 210) and developed by Zawadzki.[77] The alternative reactions involved are:

$$\begin{aligned}
&NH_3+O \rightarrow NH+H_2O\\
&NH+O_2 \rightarrow HNO_2 \rightarrow NO\\
&NH+O \rightarrow HNO \rightarrow N_2O\\
&NH+NH \rightarrow N_2+H_2\\
&NH+NH_3 \rightarrow N_2H_4 \rightarrow N_2+2H_2\\
&NH+HNO \rightarrow N_2+H_2O
\end{aligned}$$

The decomposition of HNO_2 and HNO to give NO and N_2O respectively takes place by the mechanisms proposed by Bodenstein and Wendlandt for the hydroxylamine mechanism. The main reason for preferring the imide theory is that the formation of hydroxylamine is endothermic[77, 83] and so would not occur at every collision. However, Krauss[88] calculated that the heat of adsorption of hydroxylamine is 23 kcal./mol., so that the formation of adsorbed hydroxylamine should be exothermic. Also the failure to observe significant quantities of hydrazine in the low pressure experiments[86–89] is evidence against the imide theory.[85] A final theory, due to Zawadzki (Mellor, VIII, 211) and Adadurov[90, 91] that nitrogen atoms are formed, has not received support.

The formation of nitrogen can occur by reaction of adsorbed species, as shown in the above mechanisms, or by decomposition of ammonia on parts of the platinum catalyst not covered with adsorbed oxygen or on other surfaces in the apparatus. It can also be formed by the homogeneous reaction between ammonia and nitric oxide, either beyond the gauze at high linear velocities which give some undecomposed ammonia, or before the gauze at low linear velocities which permit back diffusion of nitric oxide. The decomposition of ammonia on the walls of the apparatus has been emphasized by Polyakov,[92–95] who showed that in a quartz apparatus addition of 0·1% of hydrogen sulphide to 8% of ammonia in air increased the yield of nitric oxide by inhibiting the decomposition of ammonia on the quartz.[93] This effect can be important also in commercial operation, so that aluminium and aluminium–magnesium alloys (on which the decomposition rate is small) are preferred to mild steel or stainless steel as materials of construction.[96] The homogeneous reaction between ammonia and nitric oxide has an activation energy of 55 kcal./mol. and is rapid at 800–900°C.[97] This reaction explains the decrease in yield on increasing the spacing between gauzes when a number of gauzes are used in series.[98] Epshtein considers that the formation of nitrogen on the catalyst surface is due to decomposition of ammonia at points not protected by adsorbed oxygen, and does not involve oxygenated intermediates.[99] A number of other authors have discussed the mechanism of ammonia oxidation.[100–107]

Production of Nitric Acid

In the production of nitric acid the products from the oxidation of ammonia are cooled and absorbed in water; the following reactions occur:

$$\begin{aligned}
&2NO+O_2 \rightarrow 2NO_2 \text{ (in the gas phase)}\\
&3NO_2+H_2O \rightarrow 2HNO_3+NO
\end{aligned}$$

These reactions are faster at higher nitric oxide concentrations which can be achieved by the use of oxygen or increase of pressure.[108] Laboratory experiments with ammonia–air–oxygen mixtures give satisfactory operation of the burner with concentrations of 13–14% of ammonia and 27–28% of oxygen.[109–111] To obtain higher concentrations without the danger of explosion, steam may also be added to the burner mixture and condensed before the absorption step.[112, 113] Plants using steam–oxygen mixtures have operated successfully, but unless very cheap by-product oxygen is available the use of higher pressures is more economical.[96, 114] Pressures up to 8 atm. are used and although the conversion to nitric oxide may be reduced to 95–96%, compared with 97–98% at atmospheric pressure, the output per burner can be increased by as much as ten times.[114–118]

Erosion of Platinum Catalysts

During the oxidation of ammonia on platinum gauze some hydrogen is formed and dissolves in the platinum; this increases the mobility of the atoms in the crystal lattice and the ease of volatilization. Alternate oxidation and reduction of the surface break up the structure and increase the rate of erosion.[119–122] Examination by the electron microscope of a platinum foil which had been used for ammonia oxidation showed a million-fold increase in the number of peaks in the surface and a preferential development of the (100) faces.[123] Losses of platinum from the gauze are increased by the use of oxygen,[124, 125] higher temperatures,[125] pressures[126, 127] or linear velocities,[128] or by the presence of dust in the reactants.[128] The most satisfactory way to minimize catalyst losses is to use a platinum–rhodium alloy containing 5–10% of rhodium.[129–131] Pure rhodium does not absorb hydrogen[132] and the stability of the platinum–rhodium alloys is caused by their absorbing less hydrogen than does pure platinum.[131] A three-component alloy containing 92% of platinum, 5% of rhodium and 3% of tungsten is even more stable.[132] The loss in weight of 93% platinum–7% rhodium gauzes operated at 7 atm. and 880–900°C. was 5–10% in three weeks.[133] The stability of the catalyst can be increased by recrystallization by heating to 1000–1500°C.[134, 135] or by hammering, pressing or rolling.[136, 137] The catalyst is poisoned by phosphorus, sulphur, arsenic, silicon, lead, bismuth and tin, all of which form compounds with platinum. Gold, palladium, calcium, barium, magnesium, manganese, chromium, iron, cobalt and nickel reduce the yield but do not react with the catalyst. Vanadium, zirconium and beryllium have little effect on the yield but attack the gauze. Tungsten and rhenium increase the yield and also the rate of loss of catalyst.[138] Neither sulphur dioxide[139] nor any compound of carbon, hydrogen and nitrogen[140] has any poisoning effect on the catalyst, and the yield is increased by the presence of pyridine[141] or hydrogen sulphide.[142]

Following the development of the stable and active platinum–rhodium catalysts[143, 144] a number of patents describe the use of pure platinum, conjointly with platinum–rhodium.[145–150] Use has also been made of ternary alloys of platinum and rhodium with tungsten,[151, 152] iridium,[153–155] cobalt,[156] palladium[157] or various refractory oxides,[158] and of binary alloys of platinum with tungsten,[159, 160] tantalum,[159] thorium,[161] zirconium,[161] copper,[162] silver[162, 163] or nickel.[164] Platinum–ruthenium alloys containing in addition other metals may be used,[165, 166] and rhenium may be used alone or alloyed with other metals.[167, 168] The activity of platinum alloy catalysts may be increased by recrystallization by heating to temperatures above 900°C.[169] The platinum catalyst may be supported on porcelain,[170–172] alumina,[172, 173] silica,[172] chamotte,[172] pozzuolana[174] or other porous ceramic material.[175] Ammonia can be oxidized on a fluidized bed of a supported platinum catalyst.[176] Ostwald has given a historical account of the development of the platinum catalyst for ammonia oxidation.[177]

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Oxidation of Gaseous Ammonia on Oxide Catalysts

The various reaction mechanisms which have been proposed for the oxidation of ammonia on oxide catalysts are similar to those proposed for platinum. Thus Nagel considered that nitroxyl was the primary product from experiments on manganese-containing catalysts.[178] Krauss suggested that hydroxylamine was the primary product on the oxides of manganese, bismuth, barium, iron and nickel,[179] the amount of nitrous oxide formed at 300°C. depending on the quantity of excess of active oxygen contained by the catalyst.[180] Zawadzki[77] interpreted results on the oxides of copper, iron, bismuth and manganese on the basis of the imide mechanism which was applied also to experiments with cobalt oxide on alumina catalysts.[181] The oxidation proceeds *via* the lower oxides of nitrogen and not directly to nitric acid.[182] The activity of the catalysts may be determined by the equilibrium between higher- and lower-valent metal oxides,[183, 184] and lattice defects are also important, *p*-type semi-conducting oxides being more active.[185, 186] Measurements of the rate of oxidation of ammonia on a manganous oxide–bismuth oxide catalyst supported on small alumina spheres in both fixed and fluidized beds at 205–250°C. were used to distinguish transport effects in the fluidized bed from the chemical kinetic effects.[187]

At 220–440° the order of activity of various metal oxides is:

$$\mathrm{Cr} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Mn} > \mathrm{Fe} > \mathrm{V} > \mathrm{Cu} > \mathrm{Cd}$$ [188]

Up to 96% conversion to nitric oxide can be obtained at 550–700°C. over a cobalt oxide catalyst, and a maximum of 89% conversion on a mixed iron oxide–bismuth oxide catalyst.[189] Over 98% conversion of ammonia can be obtained at 710–785°C. over a catalyst prepared from water glass, aluminium sulphate, cobalt nitrate, potassium sulphate and chromium sulphate.[190]

Various methods for preparing cobalt oxide catalysts which are active for ammonia oxidation have been described.[191–195] The catalyst can be activated by digestion with hydrochloric acid,[196] a treatment which may be applied to other ammonia oxidation catalysts.[197, 198] Various promoters, including nickel oxide, may be added to the cobalt oxide catalyst,[199, 200] which may also be supported on alumina.[201] Iron oxide has been used in conjunction with platinum[202] and may be promoted by bismuth oxide,[203, 204] beryllium oxide or alumina.[205] Manganese oxide catalysts may contain the oxides of iron, bismuth or copper.[206, 207] The activity of metallic tin for the oxidation of ammonia increases on fusion owing to the formation of the oxide[208]; a mixed stannic oxide–calcium oxide catalyst gives a maximum conversion of 82% at 680°C.[209, 210] Metallic nickel gauze shows a moderate activity but soon disintegrates by oxidation.[211] Vanadium oxide catalysts have been used[212] and porous supports such as pozzuolana may be impregnated with ammonium dichromate, ammonium molybdate or manganese acetate.[213, 214] Ammonia oxidation catalysts can be prepared from non-siliceous base-exchange compounds containing a catalytically active component in either exchangeable or non-exchangeable form.[215–220] Ammonia adsorbed on activated carbon is slowly oxidized at room temperature.[221] Nitrates are obtained directly by the catalytic combustion of mixtures of ammonia and air at temperatures below 400°C. in the presence of strongly basic substances such as lime or sodium hydroxide mixed with catalysts such as nickel or cobalt oxides.[222–225] Hydrazine hydrate is formed at 100–400°C. at over 100 lb./sq. in. pressure on a silver oxide catalyst promoted with barium oxide.[226] The development of complex or mixed catalysts for the oxidation of ammonia has been reviewed by Mittasch.[227]

By passing mixtures of ammonia, methane and air over platinum gauze at about 1000°C. Andrussow obtained a 60% yield of hydrogen cyanide.[228–230] Further reference to this reaction will be found in the sub-section on uses of ammonia.

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CORROSION BY AMMONIA AND ITS HANDLING

Mild steel and cast iron have satisfactory resistance to corrosion by aqueous ammonia for many purposes,[1–3] e.g. in the condensers and the ammoniacal liquor still of a by-product coke plant[4, 5] and in steam boilers.[6–8] Indeed the presence of small amounts of ammonia decreases corrosion by sulphur compounds[9, 10] and copper salts[11, 12]; ammonia is regarded as an inhibitor of the corrosion of iron and steel.[13–15] Corrosion fatigue of steel is less in ammonia solution of pH 11–12 than in water of pH 6·8.[16] Corrosion of steel does occur with concentrated ammonium hydroxide and is not reduced by an increase in the nickel content.[17] Various corrosion inhibitors have been used, particularly in refrigeration plant, including ammonium phosphate,[18] sodium phosphate,[19] sodium chromate[20] and lead or strontium chromate.[21] Solutions in liquid ammonia are extremely corrosive, especially at elevated temperatures, and selected stainless steels must be used.[22, 23] Ammonia accelerates the corrosion of steel by town gas.[24, 25] Various stainless steels are used in high pressure ammonia synthesis plants.[26–29] At high temperatures ammonia decomposes on steel; absorption of nitrogen ensues and hardening of the surface[30] as well as corrosion.[31] The effects of ammonia on the wear[32] and erosion[33] of steel have been studied, and the influence of diffusion in ammonia corrosion has been discussed.[34]

Pure aluminium (99·99%) is attacked by normal ammonia solution in a nitrogen atmosphere.[35] In the presence of air a protective oxide film is formed[35] particularly with aluminium of normal purity (99·5%).[36, 37] The rate of solution is increased by addition of several alloying elements, particularly those of low hydrogen over-

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voltage such as platinum, iron and copper, whereas antimony and tin reduce the solution rate.[38] The rate of attack is less in concentrated ammonia.[37, 40] The protective oxide film is still formed in the presence of various ammonium salts.[41] Aluminium is not corroded by solutions of ammonium nitrate in liquid ammonia.[42] The effect of 15% ammonia, as well as other solutions, on the stress corrosion of an aluminium–zinc–magnesium alloy has been determined.[43] Aluminium is susceptible to pitting in the presence of ammoniacal liquor which contains cyanide and chloride.[44] Aluminium is used extensively for the transport and storage of ammonia.[45, 46]

Pure copper dissolves readily in air-saturated aqueous ammonia, the kinetics of the reaction showing that under many conditions the reaction rate is controlled by diffusion of oxygen to the copper surface.[47–49] In the complete absence of oxygen there is practically no corrosion of brass.[50] The corrosion of copper and its alloys, e.g. Admiralty metal, can be decreased by adding sulphur compounds, e.g. mercaptans, to the ammoniacal solution.[51] Copper powder corrodes about ten times faster in moist gaseous ammonia than in dry gaseous ammonia.[52] Corrosion by moist ammonia can be decreased by treating the powder to give a chemisorbed hydrophobic film, e.g. of a sodium soap,[53, 54] and corrosion of copper alloys can be reduced by adding ammonium fluoride.[55] The rate of solution of copper in aqueous ammonia from copper–gold alloys decreases with increasing gold concentration.[56] A 70–30 copper–nickel alloy is superior to a 90–10 alloy in resistance to ammonia.[57, 58] Ammonia attacks beryllium–copper wire.[59] The corrosion resistance to 156 chemicals of silicon-bronze and aluminium-bronze has been compared with that of pure copper and brass.[60] The presence of ammonia increases the corrosion of the copper, brass or Admiralty-metal tubes used in steam condensers.[61–64] Ammonia is partly responsible for the corrosion of copper by domestic sewage.[65]

Copper and its alloys, particularly high-zinc brasses, are susceptible to stress-corrosion cracking in the presence of ammonia.[66–68] Proper heat treatment can improve the resistance to stress-corrosion cracking,[69] but recrystallization must be avoided.[70] Intergranular corrosion of binary alloys is correlated with the change from the oriented texture of pure copper to a random orientation in the alloy.[71] Various brasses have been examined[72–74] and the mechanism of the failures investigated.[75–78] Ammonia in sea water can contribute to stress-corrosion cracking of brass propellers.[79, 80]

The corrosion of tin is probable in aqueous ammonia at temperatures above 25°C.[81, 82] The rates of solution of magnesium–cadmium and nickel–copper alloys[83] and of copper, bismuth, lead, nickel, cobalt, iron, calcium, zinc and magnesium in aqueous ammonia have been measured.[84] The presence of ammonia accelerates the oxidation by air of antimony and copper sols and retards the oxidation of lead sols; with cadmium sols the effect of ammonia changes with concentration.[85]

Glass[86, 87] and quartz[88] are attacked very slowly by aqueous ammonia and it has been suggested that apparatus for handling gaseous ammonia at high temperatures be coated with silica to prevent decomposition of the ammonia.[89–91]

The resistance of polyvinyl chloride to aqueous ammonia has been measured.[92, 93] A table gives information concerning a large number of plastics as well as metals[94] and another report gives examples of the use of different materials of construction in contact with ammonia.[87] Precautions necessary for the safe handling of liquid ammonia have been discussed.[95–99]

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USES OF AMMONIA

The consumption of synthetic ammonia for various purposes in the United States of America in 1941 and 1949 is given in Table I.[1]

Refs. p. 364

Table I.—End-use Pattern of Synthetic Ammonia in U.S.A.

	Ammonia (short tons)	
	1941	1949
Use in Fertilizers		
1 Fertilizer solutions and ammoniation	92,640	316,000
2 Sodium nitrate	79,100	42,500
3 Ammonium nitrate	—	158,000
4 Ammonium sulphate	14,760	69,300
5 Direct application	7,420	54,700
6 Uramon Cal-nitro Ammonium phosphate	—	62,000
Total	193,920	702,500
Industrial Use		
1 Industrial explosives	73,740	120,000
2 Plastics, resins, finishes	24,400	90,000
3 Sulphuric and nitric acids	33,680	58,000
4 Amines, amides, cyanides	7,340	35,000
5 Textiles (rayon, nylon etc.)	10,670	31,000
6 Nitrates and nitrites	8,250	25,000
7 Ammonium salts	14,800	20,000
8 Dyes and intermediates	11,520	20,000
9 Water treatment	—	20,000
10 Refrigeration	13,560	18,000
11 Metallurgy (nitriding etc.)	9,410	18,000
12 Petroleum refining	6,630	13,000
13 Rubber (accelerators)	2,000	5,000
14 Fermentation (yeast etc.)	1,970	3,000
15 Pigments and dry colours	810	3,000
16 Soda ash	300	3,000
17 Other industrial uses	28,300	18,000
Total	247,380	500,000
Grand total	441,300	1,202,500

In 1949 58% of the synthetic ammonia as well as most of the by-product ammonia in U.S.A. was used by the fertilizer industries. Trade statistics are also available for U.S.A. for 1945,[2] but similar information has not been published for other countries.

Ammonia used for direct application as a fertilizer may be in the form of either anhydrous ammonia[3–5] or ammoniacal liquor.[6, 7] Most of the ammonia used in fertilizers is converted into ammonium sulphate, ammonium nitrate, ammonium phosphate or urea.[7–11] Fertilizers can be made also by ammoniation of lignite,[12] peat[12–14] or other cellulosic materials.[15] Ammoniated straw,[16] sugar beet or sugar cane[17–19] is used for feeding cattle.

Ammonia has been used in refrigeration for many years (Mellor, VIII, 180); a number of papers discuss this application and compare the properties of ammonia with those of other refrigerants.[20–30]

Ammonia is used, in conjunction with chlorine, in the treatment of water.[31–33]

In metallurgy ammonia gas at above 400°C. is used to nitride iron and steel,[34–47] titanium,[48, 49] niobium,[50] tungsten and molybdenum.[51] A mixture of ammonia and a gas containing hydrocarbons is used to carbonitride steel.[52–56] Ammonia can be decomposed into nitrogen and hydrogen by passage over an iron or rare metal catalyst at about 600°C.,[57–59] and the cracked ammonia is used as a controlled atmosphere in furnaces for sintering and annealing both steel and non-ferrous alloys.[60–67] The hydrogen content of the protective atmosphere can be reduced by partial oxidation of the ammonia with air.[68–72] Cracked ammonia is used also in the hydrogenation of oils and fats.[73–75] Leaching with aqueous ammonia in the presence of air is used to dissolve nickel, cobalt and copper from sulphide ores, leaving behind iron and other impurities.[76–83] Ammonia leaching is used also with other ores containing nickel,[84–86] copper,[87–89] manganese[90] or zinc.[91] Nickel, cobalt and copper can be separated by precipitation from ammoniacal solution.[92–95] Aqueous ammonia is used for precipitating alumina,[96] for converting various metals to hydroxides[97] and in froth flotation.[98] Liquid ammonia is used to precipitate sodium hydroxide from solutions of sodium salts[99] and to purify titanium.[100] Aqueous ammonia is used in the surface treatment of aluminium,[101, 102] and of copper oxide rectifiers,[103] in brass plating[104, 105] and in the electrodeposition of tungsten alloys.[106] Ammonia is used extensively for the prevention of corrosion of iron and steel by acidic impurities.[107–123]

Liquid ammonia is used in the solvent refining of petroleum,[124–129] shale oil[130–132] and low temperature tar,[133–137] in the removal of nitrogen from natural gas[138] and in other solvent extraction processes.[139–142] Aqueous ammonia is used for the recovery of sulphur dioxide from flue gases.[143–146] The desulphurization of coke by carbonization in gaseous ammonia has been studied[147, 148] and ammoniacal liquor has been used for coke quenching.[149, 150] Treatment of ferrous sulphate with ammoniacal liquor gives a product suitable for the purification of coal gas from hydrogen sulphide,[151] a process which is assisted by the presence of ammonia in the gas.[152]

Ammonia is used in the storage and stabilization of latex,[153–159] the coloration of cherry wood,[160] the pulping of wood,[161–164] and the preparation of sensitized photographic paper.[165, 166] Ammonia is used in making resins,[167–169] in the preparation[170] and regeneration[171–173] of ion-exchange resins, and in the manufacture of rayon.[174–177] The reaction product of ammonia and phosphorus oxychloride or phosphorus pentoxide is used to make textiles and resins fire-resistant.[178–184]

Ammonia alone[185–194] or mixed with hydrogen,[195] ethane,[196] methyl ether[197] or, most frequently, acetylene[198–207] has been investigated for use as a motor fuel, particularly in Europe during the 1939–45 War. The presence of ammonia affects knocking of other fuels.[208, 209] An engine using ammonia for propelling torpedoes has been described[210] and the use of liquid ammonia as a rocket propellant has been discussed.[211–213]

Ammonia is used in the chemical industry as a raw material in the production of hydrogen cyanide,[214–221] urea,[222–227] guanidine,[228] pyrrole,[229] nitriles,[230–241] amines,[241, 242] amides,[243, 244] pyridine bases,[245] fluoromethyltriazines,[246] polysiloxaneamines[247] and phosphorus-containing additives for lubricating oils.[248] Ammonia is used also for the hydrolysis of glyceryl esters,[249] in the manufacture of soda,[250] the preparation[251] and purification[252] of sodium hydroxide, the preparation of silica sols,[253, 254] the treatment of polyhalite,[255] the dehydration of silica gel,[256] the separation of amino acids[257] and the preparation of plastics and elastomers.[258] The manufacture of nitric acid by the oxidation of ammonia will be considered in a later supplement (see also page 351).

Other actual or proposed uses of ammonia are as a constituent of cleaners,[259, 260] detergents,[261] insecticides[262] and aerosols,[263] in the preparation of active carbon,[214] neutral shellac salts[265] and starch emulsions,[266] as an anti-chlor in bleaching,[267] for gelling inorganic sols[268] and petroleum products,[269] in the production of artificial smoke,[270] for the selective plugging of petroleum reservoir sands,[271] in the determination of water in gaseous hydrocarbons[272] and as an inhibitor of the formation of hydrocarbon gas hydrates,[273] as a deflocculant of clay suspensions,[274] in the reworking of electrical porcelain bodies,[275] with hydrofluoric acid in frosting glass,[276] in the precipitation of used Friedel–Crafts catalysts[277] and the separation of suspended solid catalysts from gases,[278] in the stabilization of furfural,[279] in the suppression of triboelectricity on discharging compressed gases,[280] for detecting leakages in equipment,[281] as an extinguishing medium for benzene fires,[282] in the preparation of ^{15}N [283–186] and ^{18}O,[287] in atomic clocks[288, 289] and in proportional counters.[290]

A number of authors have reviewed the uses of ammonia.[291–296]

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SECTION VIII

AMMONIUM FLUORIDE

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Gaseous ammonia combines with hydrogen fluoride to form 'neutral' ammonium fluoride, NH_4F, and a series of 'acid' fluorides, NH_4F,xHF, where x is a small whole number. The acid fluorides are analogous to those formed by the alkali metals. Other than the fluorides, no acid ammonium halides are known.

FORMATION, PREPARATION AND PRODUCTION OF AMMONIUM FLUORIDE

Ammonium fluoride is formed when ammonia is passed into solutions of soluble fluorides. This process is often used to recover hydrogen fluoride from metal fluosilicates formed by fluoride attack on the metal silicate minerals. For example, when solutions containing magnesium fluosilicate, $MgSiF_6$, are treated with ammonia, ammonium fluoride is produced along with magnesium hydroxide and silica.[1, 2] After separation of the solids by filtration or centrifuging, the ammonium fluoride may be concentrated for use as such or treated with sulphuric acid and distilled to give hydrogen fluoride.

Processes depending on essentially the same principle have been described for obtaining titanium from ilmenite[3–5]; and from titanium, vanadium and potassium aluminosilicates.[6, 7]

When ammonium sulphate and sulphuric acid are added to fluorite in the presence of silica or silicates and the mixture is heated, ammonium fluosilicate or ammonium fluoride is produced.[2] Ammonium fluoride is also formed by treating silicon tetrafluoride with 10% ammonium hydroxide at 25–30°C.

$$SiF_4 + 4NH_4OH \rightarrow Si(OH)_4 + 4NH_4F$$

The silicic acid, H_2SiO_3,H_2O, is filtered off, and the solution of ammonium fluoride concentrated to give the acid fluoride.[8]

In the laboratory 'neutral' ammonium fluoride is prepared by passing ammonia into an aqueous solution of hydrogen fluoride and evaporating the solution over lime; the function of the lime is to prevent loss of ammonia and the subsequent formation of the acid fluoride.

The neutral fluoride may also be prepared by heating a mixture of ammonium chloride and sodium fluoride, or of ammonium sulphate and calcium fluoride; the ammonium fluoride is collected by sublimation.

Acid ammonium fluorides are prepared by heating the neutral fluoride and driving off ammonia:

$$2NH_4F \rightarrow NH_4HF_2 + NH_3$$

The compounds NH_4F,HF, $NH_4F,2HF$, $NH_4F,3HF$ and $NH_4F,5HF$ have been described.[9] NH_4F,HF crystallizes on evaporating ammonium fluoride solution at 36–40°C. Hassel and Kringstad have prepared the salt $NH_4F,2HF,0{\cdot}5H_2O$ and found it to be isomorphous with $H_2TlF_3,0{\cdot}5H_2O$.[10]

Ammonium fluoride is produced on the industrial scale by neutralizing strong hydrofluoric acid with liquid ammonia until the mixture is alkaline. The product is filtered, care being taken to avoid evaporation and the formation of an acid salt.[11] An alternative method is to pass hydrogen fluoride into a liquor containing ammonium fluoride until a solution is obtained which, on subsequent addition of ammonia and cooling, deposits crystals of ammonium fluoride. The crystals are separated and the mother liquor is re-used. By saturating the solution with hydrogen fluoride, the acid fluoride, NH_4F,HF, can also be produced by this method.[12, 13]

Other ways of producing the acid fluoride employ the reaction between gaseous ammonia and gaseous hydrogen fluoride. The gases are mixed in the correct ratio: $NH_3:HF=1:2$. Bozarth[14, 15] has developed a continuous process on this principle. The heat of the reaction is the only source of heat, and this reaches a maximum when the reactants are in the correct proportions. The product is liquid above 125°C. (m.p. of NH_4F,HF); the operating temperature is above the boiling point (240°C.).

The neutral fluoride may be converted into the acid fluoride as described above, or by heating a solution of the neutral fluoride to 100°C. to drive off water, then to about 115°C. to drive off ammonia; finally the temperature is increased to 125°C. in an atmosphere of ammonia to prevent sublimation.[16]

PHYSICAL PROPERTIES AND STRUCTURE

Ammonium Fluoride

Ammonium fluoride is a colourless crystalline solid which sublimes when heated. (Heat of sublimation, 36·1 kcal./mole[24].) The density is 1·0092 and it has a refractive index of 1·315.[25] It is a deliquescent solid readily soluble in water, the aqueous solution on electrolysis giving hydrogen at the cathode and nitrogen and oxygen at the anode.[26] The solid is almost insoluble in acetone.[27] and is slightly soluble in liquid sulphur dioxide at 50°C. under pressure[28]; it is readily soluble in hydrogen fluoride. Unlike other ammonium halides, the fluoride is almost insoluble in liquid ammonia[29]; the solution thus formed contains a 1-ammoniate, NH_4F,NH_3, which has a dissociation pressure of approximately 335 mm. Hg at $-35{\cdot}5$°C.[30]

Ammonium fluoride differs in structure from the other halides; its lattice is hexagonal and not cubic. The structure is of the wurzite (ZnO) type. Unit cell dimensions are: $a=4{\cdot}39\pm0{\cdot}4$ A., $c=7{\cdot}02\pm0{\cdot}06$ A., there being two molecules per unit cell. The fluorine atoms are at $(\frac{1}{3}, \frac{2}{3}, 0)$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$; the nitrogen atoms are at $(\frac{1}{3}, \frac{2}{3}, \frac{3}{8})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{7}{8})$.[31, 32] Each nitrogen atom is surrounded by four fluorine atoms at 2·66 A. and each fluorine atom by four nitrogen atoms, the atoms being joined by a hydrogen bond.

The H–F distance (1·66 A.) being so much greater than the covalent H–F distance (0·94 A.), the NH–F bond must be due to resonance between N^-HF^- and $N^-H^+F^-$ in each of the four N–H bonds.[33] The resonance structures are possible because of the high electronegativity of fluorine; this is borne out by the occurrence of similar bonds in hydrazinium fluoride,[34] and the absence of such bonds from other ammonium and hydrazinium halides. The presence of hydrogen bonds is indicated also by refractivity measurements,[35] and by the fact that thermal decomposition of ammonium fluoride is appreciable at 100°C., whereas other halides do not decompose appreciably below 200°C.

More recent investigations of the crystal structure of ammonium fluoride by nuclear magnetic resonance techniques indicate that the N–H distance is $1{\cdot}04\pm0{\cdot}01$ A. and the H–F distance is $1{\cdot}64\pm0{\cdot}02$ A.[36] A slightly different value for the N–H distance of $1{\cdot}025\pm0{\cdot}005$ A. is reported by Gutowsky *et al.*[37]

A change in the ion packing which occurs at the transition temperature (-27°C.) has been established by measurement of the variation of dielectric constant with temperature.[38–40]

Acid Ammonium Fluoride

Acid ammonium fluoride is a colourless crystalline solid with a refractive index of 1·21. When heated it readily sublimes. It is deliquescent and readily soluble in water, alcohol and anhydrous hydrogen fluoride.

The structure of the acid fluoride is complex owing to the presence of the HF_2^- ion which is non-spherical. An accurate three-dimensional analysis reveals that, in the HF_2^- ion, the hydrogen atom lies midway between the two fluorine atoms.[41] Crystallographic data have been published by Hassel and Luzanski[42] and revised and corrected by Pauling[43] and by Rogers and Helmholz.[44] The crystal structure is orthorhombic, pseudotetragonal, with $a_0 = 8{\cdot}426$ A., $b_0 = 8{\cdot}180$ A., and $c_0 = 3{\cdot}69$ A. The symmetry is V_h^7 in which each nitrogen atom is attached by hydrogen bonds to four fluoride ions at a distance of $2{\cdot}80 \pm 0{\cdot}025$ A., and each fluoride ion to two nitrogen atoms and one fluoride ion. The F–H distance in the linear HF_2^- groups is 1·184 A. and the F–F distance is $2{\cdot}32 \pm 0{\cdot}03$ A.

The infra-red absorption spectra of acid sodium fluoride, $NaHF_2$, acid potassium fluoride, KHF_2, and NH_4HF_2 in potassium chloride are identical, but different spectra are obtained from a Nujol mull.[45] This is thought to be due to the formation of mixed crystals in the alkali halide disks.

CHEMICAL PROPERTIES

The most important reactions of the ammonium fluorides are those in which they act as fluorinating agents. For example ammonium fluoride reacts[17] with sulphur trioxide:

$$NH_4F + SO_3 \rightarrow NH_4SO_3F$$

With phosphorus pentoxide the ammonium salt of the difluorophosphoric acid is formed[18]:

$$NH_4F + P_2O_5 \xrightarrow{135°C} NH_4PO_2F_2$$

Both the fluoride and the acid fluoride have been used to fluorinate chlorides.[19] Examples are:

$$AsCl_3 + 4NH_4F \rightarrow AsF_3 + 3NH_4Cl$$
$$CH_3AsCl_2 + 2NH_4F \rightarrow CH_3AsF_2 + 2NH_4Cl$$

Further reactions of this type carried out by Wilkins[20] include the following:

$$SiCl_4 + NH_4F \rightarrow SiCl_3F + SiF_4$$
$$PCl_3 + NH_4F \rightarrow PCl_2F + PF_3$$
$$POCl_3 + NH_4F \rightarrow POCl_2F + POClF_2 + POF_3$$
$$Et_2SiCl_2 + NH_4F \rightarrow Et_2SiF_2 + Et_2SiClF$$

Ammonium fluoride forms complexes by reaction with metal fluorides. The reaction between ammonium fluoride and metal fluorides of the type, $M^{II}F_2$, where M^{II} is a bivalent metal, has been studied.[21] When M^{II} = Ni, Co, Zn, or Cu complexes of the composition $M^{II}F_2,2NH_4F,2H_2O$ are formed; when M^{II} = Cd the product is CdF_2,NH_4F.

The complex, NH_4BrF_4, is formed in a violent reaction between ammonium fluoride and bromine trifluoride.[22]

$(NH_4)_2MnF_6$ is formed when a solution containing manganous fluoride, MnF_2, and acid ammonium fluoride is electrolysed. The corresponding iron complex is precipitated when ammonium fluoride is added to solutions of ferric chloride (or hydroxide) in hydrofluoric acid. The precipitate has the composition $(NH_4)_{2\cdot6}FeF_{5\cdot6},0{\cdot}4H_2O$. When the ammonium:iron ratio is greater than 3:1 no precipitate appears.[23]

SYSTEMS CONTAINING AMMONIUM FLUORIDE

Several systems containing ammonium fluoride have been studied. In the system NH_4F–KF–H_2O at 25°C. no double salts are formed, the solid phases being NH_4F,KF and KF,$2H_2O$.[46] The double salts $2NH_4F$,BeF_2 and NH_4F,BeF_2 have been shown to be present in the system NH_4F–BeF_2–H_2O at 0°C.,[47] and in the NH_4F–AlF_3–H_2O system at 25°C. the solubility isotherm consists of four branches corresponding to the compounds: AlF_3,$3H_2O$, NH_4AlF_4, $2NH_4F$,AlF_3,H_2O, and $(NH_4)_3AlF_6$.[48] The systems of ammonium fluoride and water and the acid fluoride and water have also been studied.[49–51]

A detailed discussion of the system of ammonium fluoride and ice and its electrical properties has been given by Zaromb.[52–54] The existence of the intense star Laue pattern observed by Lonsdale[55] in this system has been doubted.[56] There has been an extensive survey of the thermodynamic properties of the ammonium fluoride–acid fluoride system.[57, 58]

APPLICATIONS

For Cleaning Metals and Preventing Corrosion

The ammonium salts of hydrogen fluoride are used extensively for cleaning metal surfaces and for preventing corrosion. Aluminium surfaces are cleaned by immersion in molten ammonium fluoride at 300–375°F.[59] Oil stains and oxide films are removed and the surface brightened in one operation. Another process, used particularly for aluminium 'skins' for aircraft, employs an aqueous solution containing polystyrenesulphonic acid, citric acid, acid ammonium fluoride, benzenesulphonic acid, and phosphoric acid; it is claimed that the corrosion resistance of the brightened surface is considerably increased.[60]

The oxidized film on silicon steel can be removed by coating the surface with ammonium fluoride and heating in hydrogen at 600–1200°C.[61] An aqueous solution of acid ammonium fluoride containing nitric acid and fluosilicic acid is used to polish chemically alloys containing zirconium, hafnium, titanium, lead and tin.[62] This operation is particularly useful for zirconium containing carbide inclusions. Another solution which contains nitric acid and ammonium fluoride together with small amounts of ethane-1:2-diol, chromous oxide, and cupric nitrate is used in a rapid-brightening process for aluminium; the metal is immersed in the solution at 175–212°F. for three minutes.[63]

The influence of ammonium fluoride on the rate of attack on titanium by acids has been studied.[64, 65] Normally the metal is resistant to attack by acids (except hydrofluoric); addition of ammonium fluoride to other acids increases the rate of attack by liberating hydrogen fluoride. At very high concentrations of ammonium fluoride the titanium becomes passive, probably owing to the precipitation of a partial salt film on the metal surface and the increase of the hydrogen overvoltage caused by ammonium fluoride.

The fluoride is used as a soldering flux; the vapour keeps the metal surfaces free from oxides and can be swept away in nitrogen when the soldering is complete leaving no residue.[66] A solution of acid ammonium fluoride, ammonium chloride and triethanolamine in methyl alcohol and water is particularly useful as a flux in soldering galvanized surfaces.[67]

Chromium can be introduced into the surface of steel giving a bright, ductile, corrosion-resistant layer: steel parts are heated with chromium and ammonium fluoride in a reducing atmosphere and under slight pressure. Chromous fluoride, CrF_2, is produced at 210–480°F. At 1500°F. chromium is formed and diffuses into the steel. Layers up to 0·04 in. have been so produced.[68]

The corrosion of copper alloys by oxygenated ammoniacal solutions is considerably reduced by the addition of small quantities of ammonium fluoride to the solutions.[67]

The ease with which ammonium fluoride attacks silica and silicate materials makes it useful in the etching of glass[70, 71]; it is easier to handle than hydrofluoric acid. It is also a beneficial constituent of mixtures for polishing glass,[72] and, in small amounts, of any mixture designed to act as an adhesive to glass.[73]

The reaction between a metal and the steam atmosphere of the mould in which it is being cast can seriously affect the quality of the casting. Alloys containing phosphorus, magnesium, and any of the more electropositive metals are particularly susceptible to this 'mould reaction'; they become porous owing to the occlusion of gases, chiefly hydrogen. Addition of ammonium fluoride to the mould sand reduces the mould reaction considerably.[74–77]

As a Catalyst

Ammonium fluoride is a useful catalyst in the isomerization, alkylation and cracking of hydrocarbons. For isomerization and alkylation it is used with hydrogen fluoride. Operating temperatures are from 32° to 300°F. and, in the case of isomerization, elevated pressures are employed and boron trifluoride is often included as a promoter.[78–80] For catalytic cracking and reforming, anhydrous ammonium fluoride is used as a homogeneous vapour-phase catalyst. The catalyst sublimes in the presence of the oil below the active cracking temperature and passes through the system with the oil. The mixture of oil and catalyst vapours is heated to 720–820°F. until the desired conversion is effected. About 0·5 to 5% of catalyst is used in the oil.[81, 82]

For Preparing Other Compounds

Synthetic cryolite is made by adding a solution of ammonium fluoride to a solution containing sodium sulphate and aluminium sulphate; the resulting precipitate is easily filtered.[86] Neutral ammonium fluoride reacts rapidly with freshly prepared aluminium hydroxide in aqueous solution to form ammonium fluoroaluminate, $(NH_4)_3AlF_6$, which is stable; no such reaction occurs with ferric hydroxide as the fluoroferrate ion, $FeF_6^{\equiv}$, is unstable. This reaction has been used to separate phosphate ions in aluminium hydroxide gels.[87]

Ammonium fluoride (or the acid fluoride) has been used to produce other fluorides. A method for producing boron trifluoride is to heat acid ammonium fluoride with boric acid in such a ratio that there are three fluorine atoms to each boron atom. The mixture is evaporated to dryness and boron trifluoride is liberated on treating the residue with sulphuric acid.[88] Very pure beryllium fluoride, BeF_2, has been prepared by heating basic beryllium acetate with ammonium fluoride to 200–500°C.[89] Ammonium fluoride has been used in the dry refining of rare earth fluorides[90]: the fluorides, prepared by a wet process, are heated at 1100°C. with ammonium fluoride in a graphite crucible buried in carbon; a 90% yield is reported. General methods for preparing pure metal fluorides from oxides by treatment with acid ammonium fluoride and thermal decomposition of the product have been described.[91]

Pure silica, 'white soot', a valuable product for the rubber industry, is produced by treating silicates with ammonium fluoride and subsequently decomposing the resulting ammonium fluosilicate, $(NH_4)_2SiF_6$, with ammonia and water.[92]

Miscellaneous Applications

Ammonium fluoride has been employed to remove sulphur and silicon impurities from coke to be used for electrodes and in metallurgical operations,[83, 84] also to reduce scaling of equipment in the production of phosphorus.[85]

Other applications of ammonium fluoride include its use as wood preservative,[93–96] disinfectant,[97] mouthwash,[98] whitewash,[99] for bleaching textiles,[100] for increasing the current yield in the electrolytic preparation of dithionate,[101] as a constituent of salt mixtures employed in the electrolytic production of magnesium from magnesium oxide,[102] and as a device for maintaining a high pH (>7) in the flotation of iron ores.[103, 104]

A useful paper on the methods of handling ammonium fluoride solutions on an industrial scale has been published.[105]

ANALYSIS

A rapid and reasonably accurate method for titrating acid ammonium fluoride is to remove the hydrogen fluoride with neutral calcium chloride and titrate the equivalent hydrochloric acid liberated; for this purpose any common indicator may be used.[106, 107] Another method is to titrate the acid fluoride against 0·1 N. barium hydroxide solution using a common indicator. The concentration of free hydrogen fluoride varies from 29 to 33%; hence a correction table is necessary.[108]

The colorimetric silicomolybdic acid method for the determination of silicon has been adapted to the determination of small amounts of silica, present as $SiF_6^{=}$, in ammonium fluoride.[109] The interference of the fluoride ion is prevented by adding boric acid and the colour is developed by adding nitric acid and ammonium molybdate.

The use of ammonium fluoride in place of hydrofluoric acid for the decomposition of siliceous materials has been described; the ease of handling and lower toxicity are advantageous.[110–112]

ORGANIC COMPOUNDS

As in inorganic chemistry, ammonium fluoride is widely used as a fluorinating agent in organic chemistry. Acyl fluorides have been prepared directly from the carboxylic acid by treatment of the acid with non-metallic chlorides or oxychlorides in the presence of ammonium fluoride.[113] The yield is better if alkali metal fluorides are used.

Many reactions involving the fluorination of organosilicon compounds by ammonium fluoride have also been described.[114–116]

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SECTION IX

AMMONIUM CHLORIDE

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OCCURRENCE

Ammonium chloride has been found in various places where natural combustion processes have been at work on nitrogen-containing materials in the absence of water. At Tamaki in New Zealand, for example, the salt sublimes during the underground burning of lignite and is deposited on overlying clay strata.[1] Along with other ammonium salts it was found in the burning shafts in coal measures at Kladno in Czechoslovakia[2] and more recently in a lignite mine at Kelcany in the same country, mixed with allotropic modifications of sulphur,[3] and in the form of dendritic aggregates in cracks in shale overlying beds of soft coal in Mongolia that had caught fire.[4]

FORMATION AND PREPARATION

In small amounts ammonium chloride is formed in a variety of ways; for example by destructive distillation of village refuse used as fuel in baking crude bricks,[5] of the de-fatted oil cake of silkworm chrysalides,[6] and of leather scrap.[7, 8] It may be synthesized from its elements by the action of pressure and heat,[9] and may be made by heating the nitride of aluminium or silicon at about 1000° in a current of dry gaseous hydrogen chloride.[10] It is formed in reactions between nitryl chloride and liquid ammonia at $-75°$,[11] between cyanogen iodide and water catalysed with hydrochloric acid,[12] between solid tellurium dichloride and liquid ammonia,[13] and between ammonia and sulphuryl chloride.[14]

To obtain ammonium chloride in a pure form for such purposes as determinations of physical constants and the atomic weight of nitrogen, various workers have first made pure hydrogen chloride by burning purified chlorine in hydrogen, absorbing the product in distilled water and fractionally distilling the aqueous acid so obtained, and then have combined the acid with pure ammonia derived synthetically, finally subliming the ammonium chloride several times.[15, 16]

MANUFACTURE

Apparently the simplest way to manufacture ammonium chloride would be to neutralize ammonia with hydrochloric acid, either in the gaseous phase or in aqueous solution. The literature indeed contains many references to proposed methods for this neutralization, but they have not found general use and they contribute insignificant tonnages to the total ammonium chloride of commerce. The reasons for their unsuitability are mainly economic since other methods exist that are more convenient and cheaper to operate, particularly in respect of plant corrosion.[17–30]

The ammonia formed during the carbonization of coal in gas works and coke ovens appears in the various aqueous condensates partly as free ammonia, partly as ammonium salts including the chloride, and this might suggest itself as a source of the material. Methods of extracting ammonium chloride as such from these liquors and of converting the other ammonium compounds present into the chloride are known,[31–47] but they are little used mainly because, owing to the presence of other compounds (particularly organic nitrogen compounds and sulphides) in the liquors, it is almost impossible for these methods to give ammonium chloride both white and pure enough for commercial use. But where, as in Britain, gas-works ammoniacal liquors provide the make-up ammonia for the ammonia–soda process, it is this ammonia that ultimately appears as the ammonium chloride of commerce, for this, as will be seen, is nowadays almost entirely obtained as a by-product from a portion of the ammoniacal end-liquors of the ammonia–soda process. In countries, for example the U.S.A., where make-up ammonia for the ammonia–soda process is often synthetic in origin, much of the ammonium chloride will have derived its nitrogen from the air and not from mineral sources.

One can thus in general say that ammonium chloride of commerce is made by double decomposition processes in which phase-rule principles are applied to precipitate it from aqueous solutions containing ammonium ions, chloride ions and other ions usually of sodium, calcium, sulphate and sulphite. Of these processes that linked to the ammonia–soda process accounts for all British production and most of that abroad, and deserves first consideration. Other processes based on (*a*) modified ammonia–soda processes such as those in which solid sodium chloride is employed as distinct from saturated brines, (*b*) reactions between ammonium sulphate or ammonium nitrate and sodium chloride, (*c*) reactions between ammonium sulphite and sodium chloride, also merit discussion.

The Ammonia–Soda Process

The standard process may be represented by the equations:

$$CO_2 + NH_3 + H_2O \rightarrow (NH_4)HCO_3$$
$$(NH_4)HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$$

from which ammonium chloride appears to be an end-product. In practice in the process proper it is never isolated but remains in solution and is distilled with milk of lime in order to recover its ammonia for recycling:

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

To obtain solid ammonium chloride it is necessary to divert a portion of the solution and subject it to various treatments. The solution, which is in effect the mother liquor left after the precipitated sodium bicarbonate has been filtered off, contains about 20% of ammonium chloride, 8% of sodium chloride, 5% of ammonia and carbon dioxide mainly in the form of ammonium bicarbonate and less than 1% of sodium bicarbonate. The object is to precipitate ammonium chloride selectively, uncontaminated with sodium bicarbonate, and this is achieved by adding ammonia and powdered salt and cooling below room temperature. Ammonium chloride crystallizes out and is separated from the liquor by centrifuging. By careful control of the temperature sodium bicarbonate (although present in supersaturation) does not normally crystallize, but if there should be any danger of its doing so the liquor may be carbonated after the addition of ammonia and salt in order to precipitate and remove sodium bicarbonate first. Many variations of this basic process have been described.[48–76]

The literature contains several references to modified ammonia–soda processes (none of which, however, is in significant commercial use) whose object is to produce ammonium chloride in amount equivalent to the sodium bicarbonate, all the ammonia in the cycle thus leaving it as ammonium chloride. Two of these processes are of interest. In one[77–79] the problem of avoiding co-precipitation of ammonium chloride and sodium bicarbonate is attacked by adding to the liquors a readily soluble ammonium or sodium salt, such as the nitrate, thiocyanate or formate, which remains in solution throughout the cycle with the object of lowering the solubilities of sodium bicarbonate and ammonium chloride so that in a first stage all bicarbonate ions are removed from solution as sodium bicarbonate and in a second all ammonium ions as ammonium chloride. This process did not achieve lasting success because in practice ammonium chloride does not crystallize out sufficiently free from sodium chloride or bicarbonate. In the other process,[80, 81] which is cyclic and was the result of a penetrating study of the system [Na,NH_4]–[HCO_3,Cl]–H_2O, two stages are operated: (i) more carbon dioxide is added to a liquor containing sodium chloride, ammonia and carbon dioxide at 20–40° and causes precipitation of sodium bicarbonate only; (ii) ammonia and sodium chloride are added to the filtrate in sufficient amount at 0–10° to precipitate ammonium chloride only, the mother liquor being recycled to the first stage. Similar processes are described in more recent literature.[82, 83]

Ammonium Sulphate–Sodium Chloride Process

In aqueous solution sodium chloride and ammonium sulphate undergo double decomposition according to the equation:

$$2NaCl + (NH_4)_2SO_4 \rightarrow 2NH_4Cl + Na_2SO_4$$

Various proposals have been made for realizing this reaction on a manufacturing scale; in most of them hot solutions of the two reactants at chosen concentrations are mixed. Sodium sulphate crystallizes first and leaves the ammonium chloride in the mother liquors which are concentrated by evaporation; on cooling ammonium chloride crystallizes out and is freed from any residual sodium sulphate by washing on the filter.[84–88] Variations of the sulphate process have been described in the patent literature; these have little industrial significance, but possess chemical interest as examples of ionic equilibria.[89–92]

Ammonium Sulphite–Sodium Chloride Process

The essential reaction may be represented by the overall equation:

$$2NH_3 + H_2O + SO_2 + 2NaCl \rightarrow Na_2SO_3 + 2NH_4Cl$$

but it takes place in two stages, firstly the formation of ammonium sulphite from ammonia, sulphur dioxide and water, and secondly the double decomposition between ammonium sulphite and sodium chloride. The operation of a process based on the reaction, and the phase rule investigations preceding it, have been described[93] and there are other references in the literature.[94–96]

Ammonium Nitrate–Sodium Chloride Process

The remaining group of processes deserving mention is based on double decompositions between ammonium nitrate and sodium or potassium chlorides according to the equation:

$$NH_4NO_3 + Na(K)Cl \rightarrow NH_4Cl + Na(K)NO_3$$

It is doubtful whether this process has ever emerged from the patent literature into actual practice. In spite of this the references are useful in connection with the application of phase-rule principles to the separation of molecular species from multicomponent systems.[97–111]

Miscellaneous Processes

Miscellaneous processes based on double decompositions between soluble chlorides other than sodium chloride, for example calcium chloride, and other soluble ammonium salts, for example ammonium oxalate, are the subject of patents,[112–119] as also are processes involving the use of base-exchange materials.[120, 121] Whilst these contain some interesting chemistry they make only a negligible contribution to the world's annual production of approximately a hundred thousand tons of ammonium chloride.

All wet processes for making ammonium chloride depend ultimately for success on their ability to ensure precipitation of the salt contaminated as little as possible with other salts. Where particular ionic equilibria make this difficult to achieve by solubility relationships alone other techniques may be invoked, for example that of flotation, for it has been found that ammonium chloride lends itself readily to separation by this means from such salts as alkali metal nitrates and bicarbonates.[122–130]

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PHYSICAL PROPERTIES OF SOLID AMMONIUM CHLORIDE

Crystal Structure and Habit

Ammonium chloride crystallizes in the cubic system and is dimorphous. There is an upper transition point at 184·5° below which the structure is that of the cæsium chloride (8:1) body-centred lattice, whilst above this temperature it is that of the sodium chloride (6:1) face-centred lattice. There is also a lower transition point at −30·5°, usually referred to as the λ-point, at which an intramolecular re-orientation occurs, and though the crystal retains its cubic cæsium chloride-type lattice it becomes piezo-electric and in some way less symmetrical.

The unit cubic cell contains one molecule of NH_4Cl and has an edge-length of 3·866 A.[1–4]; around each nitrogen atom the four hydrogen atoms are arranged tetrahedrally, and the eight equidistant chlorine ions at the corners of a cube; the distance H–N has been determined by electron-diffraction[5] by neutron-diffraction[6, 7] and by nuclear magnetism measurements[8] to be very nearly 1 A. Measurements of the polarization of Raman rays seem to indicate that the NH_4^+ ions have not the same orientation in NH_4Cl as in NH_4I and that the axes of symmetry of the NH_4 tetrahedron are not parallel to the cyrstallographic axes.[9] *X*-Ray analysis has shown that in tetradeuterammonium chloride, ND_4Cl, above the λ-point the unit cell dimension is equal within experimental error to that for NH_4Cl, but that at much lower temperatures, for example −78°, it is a few thousandths of an A. greater.[10]

Transitions

The heat of transition at 184·5° has been determined by more than one worker, and there is some disagreement among the reported values which range from about 950 to 1050 g.-cal./g.-mol.[11] Intensive drying of the salt has no effect on the transition.[12]

The λ-point transition is discontinuous, i.e. isothermal in its closing stages and exhibits a hysteresis loop about 0·3° wide.[13–17] This provides an interesting contrast with tetradeuterammonium chloride, ND_4Cl, which has a λ-point at −23·4° where it undergoes continuous transition without hysteresis.[18–20] The partly deuterated

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ammonium chlorides NHD_3Cl and NH_3DCl on the other hand do exhibit some hysteresis at their respective λ-points of −25·2° and −28·7°, though the widths of the loops are less than 0·3°.[21] The dielectric constant of ammonium chloride falls abruptly as the salt is cooled through the λ-point and hysteresis effects can be observed[22–25]; the piezo-electric effect sets in at the same point and by −32·5° it has attained its full low-temperature value.[26] Ammonium bromide, with which ammonium chloride forms a complete series of solid solutions, exhibits a λ-point at −38·6° but contracts on passing from the low-temperature form to the room-temperature form, whereas ammonium chloride expands. The solid solutions show bromide-like or chloride-like transitions depending on the proportions of the two salts, there being also a relatively small range of compositions over which both types of transition occur.[27–30]

Gradual transitions in molecular and ionic solids have been observed not only in ammonium chloride, which provided the first example to be definitely characterized, but also in other ammonium salts and in many condensed gases and organic compounds. One theory to account for their existence was that they mark a change from librational oscillations of molecules or ions below the λ-point to relatively free rotations in the crystal lattice above it, and this simple hypothesis suffices to account for the observed rise in dielectric constant and fall in specific heat as the temperature rises through the transition point. On the other hand, experimental evidence with some solids can be explained only by assuming that librational oscillations persist on both sides of the λ-point, and that an increase in disorder occurs as the temperature rises through the point, which is due not to a change from librational to free rotational oscillations but to one from librational oscillation about ordered axes to librational oscillation about disordered axes. For ammonium chloride there is indeed strong evidence that the NH_4 ions exhibit torsional oscillations both above and below the λ-point; this evidence arises from measurements of Young's modulus and of the modulus of rigidity of rods of the compressed salt and of its coefficient of expansion, from calculations of entropy changes associated with the transition, from infra-red spectra, and particularly from neutron-diffraction measurements. Above the λ-point the torsional oscillations are considered to occur in two orientations, of approximately equal energy, between which the NH_4^+ ions are randomly distributed. These orientations are the two that are possible for a tetrahedron in a cubic cage of eight chloride ions. In the one the N–H links of the NH_4^+ tetrahedron are directed towards four chloride ions situated at alternate corners of the lattice, in the other towards the remaining four. Below the λ-point only one orientation is occupied and consequently the transition consists of a change from relative order to relative disorder of the equilibrium orientations of the NH_4^+ ions.[31–40] Hitherto the question of what oscillatory changes occur at the upper transition point, 184·5°, does not appear to have been answered.

The normal habit of ammonium chloride crystals, namely cubes, octahedra and trapezohedra, may be changed by the presence of other substances in the solution from which crystals grow. For example, zirconyl and cadmium ions are particularly effective in concentrations of 0·001–0·5 mol.-% in encouraging the growth of larger and more transparent crystals and the appearance of new faces.[41–43] Cadmium and zirconyl ions, as well as those of titanium, lead, ferrous iron and chromium, are also reported to cause the development of star-like crystals[44]; the small cubes first formed become pyramidal, and the base of the pyramid extends diagonally to give star-shaped structures. Other compounds that encourage the formation of large crystals of ammonium chloride are manganese chloride,[45] sodium polyphosphates,[46] and a variety of vegetable substances including pectin and aqueous extracts of grasses, roots, seeds and barks.[47–51] Pectin is also reported to encourage the formation of rounded, non-caking crystals.[52] Similar crystals may be obtained by adding to the solution about 0·1% of a chloride which forms mixed crystals with ammonium chloride, for example a chloride of manganese, iron, cobalt, nickel or copper, and providing constant agitation whilst crystallization is proceeding.[53–55] The effect of lead chloride in modifying crystal size or habit is the subject of patents.[56–58]

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Crystallization as Dendrites

Ammonium chloride has a pronounced tendency to crystallize as dendrites, particularly from solutions that are being slowly evaporated, and a considerable amount of work has been done on the effects of various dissolved substances on dendritic growth.[59–67] The tendency towards dendritic crystallization is increased by additions of gelatine, agar-agar or glycerol which function by decreasing the rate of diffusion of the dissolved salt to the growing crystal. Under these conditions crystallization is inhibited not only at and near the face centres of the normal cubes but also along the edges, thereby so accentuating the corners as to produce the spikes that are characteristic of dendritic growth. It is diminished by several cations, for example ferric iron, copper, nickel, cobalt, calcium and also by certain anions, e.g. phosphate, carbonate, sulphate, nitrate. For each ion there appears to be a limiting concentration above which dendritic crystallization is suppressed, and the crystal assumes the normal cubic shape. In this connection it is interesting to note that ammonium chloride can stabilize the cubic form of ammonium nitrate.[68] Ammonium chloride offers good examples of oriented overgrowth of the type in which the two species are not isomorphous; thus tetragonal urea grows with its (001) plane oriented in contact with faces of the cubes of ammonium chloride, even though the structures of the two are entirely different except for a formal and dimensional similarity on the planes in question.[69] Mixed crystals of ammonium chloride and cadmium chloride exhibit a striated structure, but the double salt $4NH_4Cl,CdCl_2$ does not show a clear tendency to oriented crystallization on the (001) planes.[70]

Mechanical and Thermal Properties

The density of ammonium chloride has been found to be 1·5725 at −78°, 1·589 at −195° and by extrapolation a value of 1·60 has been deduced for absolute zero.[71] From various values determined at normal temperatures a figure of 1·5274 at 25° seems to be representative, and agrees well with the value of 1·526 calculated from *X*-ray spectra data. The density of the form stable above the upper transition point of 184·5° has been calculated from *X*-ray spectra data to be 1·265.[72]

The value of the coefficient of thermal expansion depends on the temperature, and at the lower transition point of −30·5° it increases suddenly to about eight times the figure half a degree on either side. It also shows the hysteresis associated with the lower transition point,[73] though some earlier workers failed to observe the phenomenon since their temperature control was accurate only to 0·50° and the width of the hysteresis loop is not more than half of this.[74] Values found for the coefficient of linear expansion range from about 400×10^{-5} at the transition point to $2{\cdot}69 \times 10^{-5}$ over the range 0° to −20° and $1{\cdot}23 \times 10^{-5}$ over the range −100° to −120°.[3] For the coefficient of cubical expansion figures of 28×10^{-5}, 18×10^{-5} and 9×10^{-5} have been given respectively for the ranges 19° to −78°, 19° to −195°, and −78° to −195°.[71] For temperatures from 20° to 125° the equation

$$\alpha = 0{\cdot}0_{4}4916 + 0{\cdot}0_{6}2122t + 0{\cdot}0_{8}1372t^{2}$$

has been found to fit values of the linear coefficient measured by interferometric methods at different temperatures.[75]

Under pressures of the order of 2000 atmospheres ammonium chloride crystals flow together and form a solid mass having the appearance and fracture of marble.[76] Under higher pressures there are discontinuities in the slopes of the pressure/volume isotherms, for example at 0° and 3370 atmospheres and at 30° and 9390 atmospheres.[77–79] The isothermal and adiabatic compressibilities at 0° are respectively $5{\cdot}60 \times 10^{-12}$ sq. cm./dyne and $5{\cdot}54 \times 10^{-12}$ sq. cm./dyne; various other elastic constants have been measured.[80–82]

Determinations of the vapour pressure of ammonium chloride made since Mellor wrote on the subject (II, 563) have on the whole confirmed older values and typical data are given in Table I, but the results must now be interpreted on the basis of complete dissociation in the vapour phase of NH_4Cl into NH_3 and HCl. Intensive drying is without effect on the vapour pressure.

Table I.—Vapour Pressures of Ammonium Chloride[83]

Temperature, °C.	Vapour pressure, cm. Hg
254·9	5·87
277·0	12·02
303·4	27·95
320·2	47·10
328·5	58·0
335·4	70·18
341·0	80·43
346·0	89·25
352·6	108·1

The specific heat of ammonium chloride in its relation to temperature shows, like the other mechanical-thermal properties dependent on lattice-states, an abrupt change to a maximum at the λ-point. There is also a change at the upper transition point, 184·5°, though of a much less marked degree. Results of determinations of molecular heat for ammonium chloride are given in Table II.

Table II.—Molecular Heats of Ammonium Chloride[85, 86]

Temperature, °C.	Molecular heat, g.-cal.
2·6	19·6
−8·0	19·5
−18·0	19·8
−26·0	18·7
−29·1	25·4
−29·8	41·7
−30·4	177·4
−30·5	122·5
−31·3	43·1
−32·2	34·9
−42·6	21·5
−57·3	17·9
−68·7	16·7
−167·8	9·4
−253·0	0·34
50	22·1
100	24·0
150	25·3
184·5	25·6
200	21·1
250	22·8

Mixed crystals of ammonium chloride and ammonium bromide show similar anomalies though the maximum point is at a temperature higher than that for either component.[87] Various other references relate to the connection between specific heat and temperature,[88–91] and for deuterammonium chloride, ND_4Cl, a maximum has been observed at its λ-point of about −24°.[92]

The thermal conductivity of ammonium chloride has been measured under pressure,[93] and at atmospheric pressure in the neighbourhood of the λ-point; it appears to have a maximum value not at the λ-point but at some point between −73° and −35°.[94]

Optical Properties

The refractive index of ammonium chloride for the D-line is 1·63851 at 25°, and the molar refraction deduced by means of the Lorentz–Lorenz formula from values for density and refractive index is 12·59.[95] The index has also been measured at temperatures from 0° to $-200°$.[96]

The infra-red spectra have been investigated over a wide range from room temperature down to $-190°$. Between room temperature and $-50°$ three types of absorption bands attributable to the NH_4 group have been found. In the first of these, at wave-lengths of 3·2 and 7 μ, the intensity does not vary with temperature; in the second, at 3·5, 4·25, 4·45, 4·90 and 5 μ, the intensity increases considerably with decreasing temperature; in the third, between 6·8 and 6·95 μ, the intensity decreases with decreasing temperature. The bands at 5·6 and 6·95 μ show a discontinuous intensity change at $-30·5°$, the λ-point.[97] From other measurements on both NH_4Cl and ND_4Cl no indication of fine structure due to free rotation of NH_4^+ ions has been found on either side of the λ-points, but instead evidence of torsional oscillations of the ions within the lattice which supports the belief that the λ-point transition is one of order–disorder.[98, 99]

Ammonium chloride shows the Raman effect with two broad lines at 3155 and 3035 cm.$^{-1}$ and most of the characteristic frequencies found in the infra-red appear as rather broad Raman lines, though the line at 1700 cm.$^{-1}$ is very sharp.[100–102] The salt also shows *X*-ray absorption spectra; moreover below $-50°$ it is photochemically decomposed in the wave-length region of 200–600 mμ with discoloration.[103, 104]

Electrical and Magnetic Properties

The experimentally determined dielectric constant of ammonium chloride has a mean value of 6·96 and does not depend significantly on frequency.[105] A value of 7·17 has been deduced for the powdered salt,[106] and small amounts, probably unimolecular layers, of adsorbed water give rise to a sharp peak at about $-30°$ in the curve relating dielectric constant with temperature.[107]

The magnetic susceptibility has been found to lie between $-0·667 \times 10^{-6}$ and $-0·605 \times 10^{-6}$ cm. g. sec. units/g.[108, 109] and the salt remains diamagnetic down to very low temperatures.

Nuclear magnetic resonance has been investigated from room temperature down to as low as 77° K. and the results used to gain information about the structure of the NH_4Cl molecule, for example the N–H distance has been deduced as $1·025 \pm 0·005$ A. The temperature of the transition in the width of the nuclear resonance absorption lines is more than 100° below the λ-point.[110–114]

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PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS OF AMMONIUM CHLORIDE

Heat of Solution

The solubility of ammonium chloride in water is discussed later (see page 400). Ammonium chloride has a negative heat of solution in water amounting to −4·06 kcal. per mole at 0° and −3·84 at 19°, these values corresponding to a dilution of approximately 0·5 molar.[1] The so-called integral heat of solution, that is to say the heat change when one mole of ammonium chloride is dissolved to saturation, has been found to be −4·37 kcal. at 30–40°.[2] A few values, given in Table III, are available for heats of solution to different concentrations at 0°.

Table III.—Heats of Solution of Ammonium Chloride at 0° [3]

NH_4Cl, g.-mols./litre	Heat of solution, kcal./mole
0·0625	−4·64
0·125	−4·63
0·250	−4·62
0·50	−4·60
1·00	−4·57
2·00	−4·43
4·00	−4·10

Various theoretical expressions have been derived connecting heats of solution, supersaturation coefficients and limits of supersaturation.[4, 5] Heats of dilution, expressed in Table IV as heat liberated when a solution of given concentration is diluted to infinite dilution, have been determined.

Table IV.—Heats of Dilution of Ammonium Chloride Solutions[6]

NH_4Cl, g.-mols./1000 g. H_2O	Heat of dilution at 25°, g.-cal./mole NH_4Cl
0·0016	12
0·040	59
0·078	77
0·160	98
0·360	120
0·640	133
1·00	136

Mechanical and Thermal Properties

Determinations of densities of ammonium chloride solutions have been made in recent years[7, 8] not so much to supplement earlier work but rather in connection with measurements of other physical and thermodynamic properties. For example, determinations at 25° over a concentration range of 0·10–7·38 M. (saturation) were used to calculate apparent molal volumes (V) according to the equation

$$V = 35{\cdot}828 + 1{\cdot}6088\sqrt{C} - 0{\cdot}02266C$$

where C represents concentration in moles per litre.[2] Adiabatic compressibilities of ammonium chloride solutions have been determined at 25° by means of sound-velocity measurements at supersonic frequencies, and the values obtained show a remarkable correlation with the corresponding values of the partial molal volume of the solvent water.[9]

Measurements of viscosity, illustrated in Table V, have confirmed the prediction of Jones and Dole that all salts increase the viscosity of water if measured at sufficiently low concentrations, including the salts that at moderate concentrations reduce the viscosity.

Table V.—Relative Viscosities of Ammonium Chloride Solutions[10]

NH_4Cl, g.-mols./litre	Relative viscosity, $\eta_{NH_4Cl}/\eta_{H_2O}$ at 25°
0·002	1·00020
0·005	1·00031
0·010	1·00045
0·020	1·00051
0·05	1·00054
0·10	1·00036
0·20	0·99965

Ammonium chloride lowers the viscosity of water over a concentration range of approximately 0·10–2·5 M. at temperatures below 20°. Other measurements of viscosity have provided data at various temperatures up to 75°,[11–13] and typical data are given in Table VI.

Table VI.—Viscosity Coefficients of Ammonium Chloride Solutions[14]

g.-mols./1000 g. H_2O	Viscosity coefficient × 10^3			
	0°	10°	30°	75°
1	16·879	12·554	8·067	3·988
2	16·013	12·258	8·094	4·149
3	15·516	12·029	8·116	4·280
4	15·119	12·022	8·274	4·455
5	14·985	12·093	8·399	4·542

A few measurements of surface tension, exemplified in Table VII, have been made since 1920, and some of the values, together with viscosities, have been used in testing modern theories of electrolytes.[15–17]

Table VII.—Surface Tensions of Ammonium Chloride Solutions[18]

NH_4Cl, g.-mols./1000 g. H_2O	Surface tension, dynes/cm. at 25°
2·0	74·48
4·0	76·78
6·0	78·71
7·4	80·06

Vapour Pressure, Boiling Point, Freezing Point and Specific Heat

Vapour pressures of saturated solutions of ammonium chloride, given in Table VIII, have been measured at a number of temperatures between 19° and 30°.

Table VIII.—Vapour Pressures of Saturated Solutions of Ammonium Chloride[19]

Temperature, °C.	Vapour pressure, mm. Hg
19	12·95
20	13·90
21	14·83
22	15·78
23	16·79
24	17·80
25	18·84
26	19·91
27	21·03
28	22·20
29	23·42
30	24·66

Other vapour pressure data are given in Table XXI (see page 397) in connection with activity coefficients. The literature records data for partial pressures of ammonia and carbon dioxide over ammonium chloride solutions; these have a bearing on the ammonia–soda process and the recovery of ammonia from coal gas in the form of aqueous solutions.[20–22] Measurements with supersaturated solutions of ammonium chloride at different temperatures up to 45° show no abrupt change in the vapour pressure–temperature curves as the region of supersaturation is reached.[23] Determinations of vapour pressures over supersaturated solutions in the temperature range 25–60° have been used to determine the activity of the water.[24]

Measurements of boiling point elevation have given values that show close agreement with earlier work.[25] Highly accurate measurements of the depression of the freezing point over a concentration range of 0·001–1·0 moles/1000 g. H_2O, given in Table IX, have been made in order to determine activity coefficients. It appears that dilute solutions of ammonium ions can be studied accurately only by freezing point determinations; a factor similar in effect to that of association operates with ammonium salts but is negligible with other uni-univalent salts.[26, 27]

Table IX.—Freezing Point Depression of Ammonium Chloride Solutions[26]

NH_4Cl, g.-mols./1000 g. H_2O	Molecular depression of freezing point, °C.
0·001	3·663
0·005	3·596
0·01	3·563
0·02	3·529
0·05	3·473
0·10	3·423
0·50	3·315
1·0	3·300

Specific heats of ammonium chloride solutions, illustrated in Table X, have been determined over a range of concentrations at various temperatures. The partial molal heat capacity at infinite dilution has been deduced as $-13{\cdot}2$ g.-cal./degree/mole at 25°, and there is evidence for the assumption that this is made up of equal contributions from ammonium and chloride ions.[28–30]

Table X.—Specific Heats of Ammonium Chloride Solutions[28, 29]

NH_4Cl, g.-mols./1000 g. H_2O	Specific heat, g.-cal./g.								
	20°	21°	25°	30°	35°	40°	41°	70°	86°
1·66		0·8397					0·8543		
2·00	0·8904		0·8915	0·8925	0·8936	0·8946			
3·28		0·7496							
4·00							0·7759	0·7736	
6·00									0·7093

Data are available for thermal conductivity[31, 32] and thermal diffusion.[33–38] Measurements of other miscellaneous physical properties of ammonium chloride solutions include absorption of supersonic waves,[39–41] osmotic pressure[42] and electrostriction.[43, 44]

Optical Properties

The refractive indices of solutions of various concentrations have been determined by various workers[45–49] and empirical equations deduced to relate indices to concentrations, for example

$$R = (\phi+\pi)\times\text{constant}$$

where R is the equivalent refractivity, ϕ is a single function of the density and concentration of the solution, and π is a function of refractive index and concentration.[46] Selected data are given in Tables XI and XII.

Table XI.—Refractive Indices of Ammonium Chloride Solutions at 20°C.[48]

NH_4Cl, g./100 g. solution	Refractive index at 20°	
	D-line (5890 A.)	*C*-line (6563 A.)
5·26	1·34304	1·34080
8·12	1·34839	1·34620
10·70	1·35328	1·35120
11·14	1·35415	1·35200
14·35	1·36023	1·35808
19·13	1·36926	—

Table XII.—Refractive Indices of Ammonium Chloride Solutions at 25° and 45°C.[46, 47]

NH_4Cl, g.-mols./1000 g. H_2O	Refractive index for He-line (5876 A.)	
	25°	45°
1·1619	1·3486	—
1·8774	1·3501	—
1·8916	—	1·3475
2·5178	—	1·3525
2·2680	1·3532	—
3·6504	1·3638	—
4·1464	—	1·3644
4·5897	1·3700	—
4·6914	1·3708	—
6·484	1·3814	—
6·7500	1·3830	—
6·7529	—	1·3802

The molar refractivity at infinite dilution is of the order of 13·37.[46, 47]

The magnetic rotation of the plane of polarized light (Faraday effect) and the related Verdet constants have been measured in both the visible and the ultraviolet regions of the spectrum for different ammonium chloride concentrations.[50–53] Measurements of the light scattering (Rayleigh effect) of ammonium chloride solutions have been made by several workers over a number of years, and the results compared with theoretical values derived from the Einstein–Debye theory. The differences between experimental and theoretical values may be correlated with the solvation of the ammonium ion calculated from ionic radii in solution and in the crystal lattice. For ammonium chloride the experimental is always less than the theoretical scattering, though the differences are not large.[54–59]

Electrochemical Properties

The absolute entropy of the chloride ion has been determined from electromotive force measurements in thermocells containing ammonium chloride as electrolyte and silver/silver chloride electrodes, the solution around the anode being at one temperature and that round the cathode at another. By operating at temperatures of 0° and 25° in such cells entropy values at the mean temperature of 12·5° have been calculated to be 27·9, 22·4 and 19·8 g.-cal. per degree per mole-ion respectively in 0·01, 0·25 and 1·0 M. solutions.[60] Thermocells containing silver/silver chloride electrodes have also been used to derive values for the Soret coefficient.[61, 62]

Potentials across phase boundaries between solutions of ammonium chloride in water and in various non-aqueous solvents, such as alcohols and other organic hydroxy compounds, have been determined during investigations into dielectric constants and ionic partition coefficients. A typical cell used may be represented by:

$$\mathrm{Hg/HgCl|KCl\ aq.|KCl\ non\text{-}aq.|NH_4Cl\ non\text{-}}\underset{\longleftarrow}{\overset{\longrightarrow}{\mathrm{aq.\|NH_4Cl}}}\mathrm{\ aq.|KCl\ aq.\ satd.|KCl\ aq.|HgCl/Hg}$$

The concentration of ammonium chloride in the non-aqueous phase was such that the electrical conductivity of that phase was substantially equal to that of the potassium chloride non-aqueous phase; by this means potential differences between the two non-aqueous phases were considered to be virtually eliminated. In each example in Table XIII the non-aqueous phase was positive with respect to the aqueous.

Table XIII.—Phase-Boundary Potentials Between Ammonium Chloride Solutions[63–65]

NH_4Cl, g.-mols./litre	Non-aqueous solvent	Phase-boundary potential
0·312	*n*-butyl alcohol	17 millivolts at 25°
0·450	,, ,,	15 ,, ,, ,,
0·360	amyl alcohol	21·7 ,, ,, 18°
0·600	furfurol	2·0 ,, ,, 25°
0·050	benzyl alcohol	6·0 ,, ,, ,,
0·600	phenol	6·0 ,, ,, ,,

Saturated solutions of ammonium chloride may be used to eliminate liquid–liquid junction potentials provided the pH of the environment is low enough to avoid liberation of ammonia.[66]

Determinations of the transport number of the NH_4^+ ion by the moving boundary method have given values, quoted in Table XIV, somewhat lower than those quoted by Mellor (II, 571).

Table XIV.—Transport Numbers of Ammonium Ion in Ammonium Chloride Solutions[67]

NH_4Cl, g.-mols./litre	Transport number of NH_4^+ at 25°
0·01	0·4907
0·02	0·4906
0·05	0·4905
0·10	0·4907
0·20	0·4911

The equation

$$\frac{1}{t} = \frac{1}{t_0} + A\sqrt{C} - BC$$

proposed for transport numbers, in which t_0 represents the value at infinite dilution, C the concentration in equivalents per litre and where A and B are constants, is generally applicable to ammonium chloride for values of C over the range 0·01 to 0·20.[68]

The specific conductivities of ammonium chloride solutions, given in Tables XV and XVI, have been measured at 0° and also at temperatures up to 306°; apart from these measurements little has been done in the field since the classic work of Kohlrausch, H. C. Jones and their collaborators at 18°.

Table XV.—Electrical Conductivities of Ammonium Chloride Solutions at 0°*C.*

NH_4Cl, g.-mols./litre	Specific conductivity × 10^6 at 0°	Equivalent conductivity at 0°
	mhos	mhos
0·000602	48·16	80·0
0·00387	304·4	78·6
0·00794	615·6	77·5
0·01286	985·5	76·6
0·02470	1856	75·2
0·05041	3690	73·3
0·1005	7120	71·3

Table XVI.—Electrical Conductivities of Ammonium Chloride Solutions from 18° *to* 306°*C.*[70, 71]

NH_4Cl, g.-mols./litre	Equivalent conductivity in mhos									
	18°	20°	25°	40°	60°	90°	100°	156°	218°	306°
0·002	126·5	—	146·7	—	—	—	399	601	801	1031
0·010	122·5	125·5	141·7	189	249	343	382	570	758	925
0·0125	121·5	—	—	—	—	—	379	567	—	—
0·03	118·1	—	—	—	—	—	—	—	—	828
0·10	—	113·1	—	177	235	—	—	—	—	—
1·0	—	101	—	147	194	250	—	—	—	—

Data are also available for 10° over a concentration range of approximately 0·0005 to 1·37 M.,[72] and for 25° at concentrations up to over 5 M.,[73] the latter being illustrated in Table XVII.

Table XVII.—Electrical Conductivities of Ammonium Chloride Solutions at 25°*C.*[73]

NH_4Cl, g.-mols./litre	Equivalent conductivity
	mhos
0·1019	128·6
0·2015	123·8
0·5019	116·8
1·011	111·2
2·005	105·1
3·006	100·2
4·005	95·1
5·252	87·9

Expressions for conductivity derived on the basis of the Onsager development of the basic theory of Debye and Hückel agree remarkably well with the experimental results given in Table XVII.

Interionic attractions in solutions of electrolytes cause observed values of osmotic pressure to be less than the ideal value. The ratio of the observed to the ideal osmotic pressure is defined as the osmotic coefficient. It may be calculated from measurements of freezing point depression since it can be shown to be equal to $D/1{\cdot}858n$, where D is the molecular freezing point depression, and n is the number of individual ion species, 1·858 being the molar freezing point depression constant for water. For a uni-univalent electrolyte, where $n=2$, it becomes $D/3{\cdot}716$. By measurements of freezing point depressions the coefficients recorded in Tables XVIII and XIX have been determined for ammonium chloride over the concentration range 0·001–1·00 g.-mols./1000 g. H_2O.

Table XVIII.—Osmotic Coefficients of Ammonium Chloride Solutions from Freezing Point Depressions[72]

NH_4Cl, g.-mols./1000 g. H_2O	Osmotic coefficient
0·001	0·986
0·005	0·968
0·01	0·959
0·02	0·949
0·05	0·935
0·10	0·921
0·50	0·892
1·00	0·888

Osmotic coefficients may also be calculated from measurements of vapour pressure lowering. Isopiestic vapour pressure techniques have been used over the concentration range 0·10–7·39 M.:

Table XIX.—Osmotic Coefficients of Ammonium Chloride Solutions from Vapour Pressure Measurements[75]

NH_4Cl, g.-mols./litre	Osmotic coefficient
0·10	0·927
0·50	0·899
1·00	0·897
1·4	0·900
1·8	0·906
2·0	0·909
2·5	0·918
3·0	0·926
3·5	0·936
4·0	0·945
5·0	0·953
5·5	0·963
6·0	0·960
7·39 (saturation)	0·977

Activity Coefficients

Measurements of freezing point depressions have been used to determine activity coefficients at about 0°, whilst at 25° two sets of data are available, one from vapour pressure measurements by a dynamic method, the other by the isopiestic vapour pressure method. As shown by Tables XX, XXI and XXII the two sets of results differ by about 8% over most of the range studied; those obtained by the isopiestic method are perhaps to be preferred.

Table XX.—Activity Coefficients of Ammonium Chloride Solutions near 0°C. from Freezing Point Measurements[72]

NH_4Cl, g.-mols./1000 g. H_2O	Activity coefficient—f.p. data
0·001	0·961
0·005	0·911
0·01	0·880
0·02	0·845
0·05	0·790
0·10	0·742
0·50	0·619
1·00	0·572

Table XXI.—Activity Coefficients of Ammonium Chloride Solutions at 25°C. from Vapour Pressure Measurements by Dynamic Method[74]

NH_4Cl, g.-mols./litre	Activity coefficient at 25°	Vapour pressure at 25° by dynamic method
		mm. Hg
0·10	0·765	23·67
0·20	0·721	23·59
0·40	0·686	23·43
0·60	0·668	23·28
0·80	0·655	23·12
1·0	0·646	22·97
2·0	0·617	22·21
3·0	0·605	21·46
4·0	0·603	20·71
5·6	0·604	19·97
7·39 (saturation)	0·611	18·28

Table XXII.—Activity Coefficients of Ammonium Chloride Solutions at 25°C. from Isopiestic Vapour Pressure Data[75]

NH_4Cl, g.-mols./litre	Activity coefficient
0·10	0·770
0·50	0·649
1·00	0·603
1·40	0·584
1·80	0·574
2·0	0·570
2·5	0·564
3·0	0·561
3·5	0·560
4·0	0·560
4·5	0·561
5·0	0·562
5·5	0·563
6·0	0·564
7·39	0·566

It is interesting to note that up to about 2 M. the activity coefficients for ammonium chloride are almost indistinguishable from those for potassium chloride, which suggests that the ammonium ion in aqueous solution has very much the same effective size and possibly the same solvation as the potassium ion. Data available in the literature for the solvation of ammonium chloride differ widely,[76–79] as indeed they do for some other salts, because some methods measure what has been called primary solvation whilst others measure primary and secondary solvation. Primary solvation refers to solvent molecules so firmly bound to an ion that they move with it as one unit during its Brownian motion, whilst secondary solvation refers to molecules electrostatically influenced by the primarily solvated ion in such a way that they affect such properties as salting out. Observed secondary solvation will thus depend on the method used to measure it. For ammonium chloride the primary solvation (hydration) determined from dielectric constant measurements is of the order of 4 ± 1,[80] whilst the secondary may, depending on concentration, be two or three times this value.

Activity coefficients and ionic distributions of ammonium chloride in various ion-exchange resins in contact with solutions of the salt have been measured.[81–85]

Hydrolysis

Being a salt of a weak base and a strong acid ammonium chloride is hydrolysed in

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its aqueous solutions to the acid side of neutrality. The pH values of solutions made up in water containing the usual amounts of dissolved carbon dioxide lie between about 5·3 and 5·6 over the concentration range 0·1–0·001 M. at room temperature, but the effect of the carbon dioxide on the values is significant as may be seen from the data determined by glass electrode techniques at 15°–16 given in Table XXIII.[86–89]

Table XXIII.—Hydrogen Ion Concentrations of Ammonium Chloride Solutions[87, 88]

Litres per g.-mol.	pH	
	CO_2-free water	Water containing dissolved CO_2
1000	6·51	5·63
600	6·36	—
500	6·31	—
400	6·24	—
250	6·14	—
200	6·07	—
100	5·92	5·55
50	5·75	5·49
20	5·56	—
10	5·42	5·34

Electrolysis

Depending on the current density, concentration, temperature, and the time and intensity of illumination, it is possible to identify chloramine NH_2Cl, dichloramine $NHCl_2$, nitrogen trichloride NCl_3, ammonia, ammonium hydroxide, nitrogen, chlorine, oxygen and perchloric acid in and over solutions of ammonium chloride after electrolysis. High current densities, temperatures below about 40°, high concentration and absence of light encourage the formation of nitrogen trichloride.[90] Chlorine liberated at the anode is found to react with surrounding ammonium chloride to give in the first place chloramine and hydrochloric acid, the former decomposing at high temperatures to give nitrogen, ammonium chloride again and hydrochloric acid, whilst at low temperatures it decomposes into nitrogen, ammonium chloride and chlorine.[91] Small quantities of oxygen are always found at the anode owing to discharge of some hydroxyl ions. Provided the solution contains appreciable quantities of sodium chloride, it has been possible to obtain ammonia, ammonium hydroxide and chlorine in a cell containing a steel cathode and carbon anodes with a diaphragm of asbestos paper, using current densities of the order of 12 amp./sq. dm. and a solution temperature of 50–75°. Anode and cathode efficiencies of the order of 80% were reached under such conditions but over 35% of the liberated chlorine entered into side reactions.[92] Prolonged electrolysis over several hours using graphite cathodes and platinum anodes with high current densities yields in the end a strongly acid solution containing perchlorate ions but no ammonium ions.[93, 94]

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AQUEOUS SYSTEMS CONTAINING AMMONIUM CHLORIDE

NH_4Cl–H_2O

A saturated solution of ammonium chloride boils at 114·8° under a pressure of 760 mm. Hg and contains 46·6% NH_4Cl by weight. Workers have determined the solubility above this temperature by heating the salt and water in sealed glass tubes and observing the temperature at which the system became homogeneous[1–3]; the results are given in Table XXIV.

Table XXIV.—Solubilities of Ammonium Chloride in Water from 129° *to* 417°C.[3]

Temp., ° C.	129	142	164	191	211	236	267	294	318	339	377	417
NH_4Cl, g./100 g. sol.	48·9	51·1	54·6	59·1	62·4	66·2	70·4	74·5	77·8	80·2	86·6	90·8

The effect of pressure on the system NH_4Cl–H_2O–ice is to lower the eutectic temperature for NH_4Cl–ice I from its value of −15·8° under normal pressure to −34·4° under a pressure of 2215 atm., which corresponds to a quadruple point between saturated solution, NH_4Cl, ice I and ice III′. Increase of pressure beyond this point results in a slight increase in the eutectic temperature for the system NH_4Cl–H_2O–ice III′.[4]

NH_4Cl–ice I			
Temperature, °C.	−17·5	−22·5	−32·4
Pressure, atm.	350	1190	2028

NH_4Cl–ice III′					
Temperature, °C.	−32·5	−31·2	−29·4	−29·1	−28·0
Pressure, atm.	2410	2520	2800	2890	3130

Table XXV.—System NH_4Cl–NH_3–H_2O *at* 0° *to* 75°*C.*[5]

Molar Percentage			Temperature	Solid Phase
NH_3	HCl	H_2O		
8·62	8·24	83·14	0°	NH_4Cl
9·11	8·21	82·68		"
9·59	8·18	82·23		"
13·34	8·15	78·51		"
20·69	8·08	71·23		"
29·04	8·02	62·94		"
10·82	10·48	78·70	25°	"
11·37	10·47	78·16		"
12·01	10·42	77·57		"
16·16	10·32	73·52		"
20·89	10·22	68·89		"
26·13	10·15	63·72		"
38·33	9·96	51·71		"
13·71	12·58	73·71	50°	"
15·53	12·36	72·11		"
19·27	12·25	68·48		"
16·12	14·73	69·15	75°	"
17·99	14·42	67·59		"

Table XXVI.—System NH_4Cl–NH_3–H_2O *below* 0°*C.*[5]

Molar percentage			Temperature	Solid phase
NH_3	HCl	H_2O		
4·62	—	95·38	−6·4°	ice
6·98	2·58	90·44	−12·3	"
9·06	4·89	86·05	−16·7	"
10·10	—	89·9	−13·8	ice
10·72	0·78	88·50	−15·7	"
11·13	1·52	87·35	−16·8	"
12·51	3·03	84·46	−20·8	"
17·63	—	82·37	−27·1	ice
18·39	1·09	80·52	−29·1	"
19·05	2·19	78·76	−33·1	"
24·33	—	75·67	−46·5	ice
24·98	1·16	73·86	−49·6	"
11·86	7·96	80·18	−2·7	NH_4Cl
10·69	6·67	82·64	−13·7	"
10·48	6·45	83·07	−15·09	"
15·77	7·11	77·12	−8·2	NH_4Cl
14·87	5·97	79·16	−15·6	"
20·48	4·32	75·20	−26·7	NH_4Cl
19·76	3·25	76·99	−34·1	"
26·91	5·76	67·33	−20·3	NH_4Cl
25·63	3·31	71·06	−41·5	"
10·19	5·78	84·03	−19·8	ice + NH_4Cl
13·85	4·79	81·36	−25·9	"
19·52	2·87	77·61	−36·1	"
25·21	1·58	73·21	−55·0	"
34	1	65	−115 extrapolated	ice + NH_4Cl + NH_3,H_2O

NH_4Cl–NH_3–H_2O

Equilibria in this system are important, at any rate in the lower temperature range, in the manufacture of ammonium chloride from the liquors of the ammonia–soda process. Data available extend from 0° to 75° and also from 0° down to temperatures as low as −55°. Above 0°, where the only solid phase is NH_4Cl, additions of ammonia up to about 10% by weight in the solution depress the solubility only very slightly, but above this concentration the solubility increases. Typical data are given in Tables XXV and XXVI. Below 0° there are two possible solid phases, namely NH_4Cl and ice, and extrapolation of the cryohydric curves indicates a ternary cryohydrate $NH_3,H_2O + NH_4Cl +$ ice at about −115°.[5]

NH_4Cl–HCl–H_2O

Data are available for this system in the temperature ranges 0° to 75° and 0° to −75° obtained by the workers who investigated the related system NH_4Cl–NH_3–H_2O. Data from another source for 0° and hydrochloric acid concentrations up to 44·5% HCl by weight show a decided minimum for the solubility of ammonium chloride when the HCl concentration is 33%.[6] Both sets of results are given in Tables XXVII and XXVIII.

Table XXVII.—System NH_4Cl–HCl–H_2O *at* 0° *to* 75°*C.*[5]

Molar percentage			Temperature	Solid Phase
NH_3	HCl	H_2O		
8·27	8·27	83·46	0°	NH_4Cl
7·74	8·31	83·95		,,
6·72	8·49	84·79		,,
5·80	8·79	85·41		,,
4·36	9·41	86·23		,,
3·25	10·24	86·51		,,
1·61	12·26	86·13		,,
0·80	14·29	84·91		,,
0·51	15·76	83·73		,,
0·26	18·19	81·61		,,
0·14	19·37	80·49		,,
10·47	10·47	79·06	25°	NH_4Cl
10·00	10·50	79·50		,,
9·39	10·53	80·08		,,
8·81	10·57	80·62		,,
7·57	11·06	81·37		,,
4·32	12·12	83·56		,,
2·56	14·37	83·07		,,
1·34	17·05	81·61		,,
0·92	17·82	81·26		,,
0·17	20·47	79·36		,,
12·67	12·67	74·86	50°	NH_4Cl
11·89	12·81	75·30		,,
10·99	13·15	75·86		,,
9·91	13·76	76·33		,,
7·76	14·99	77·25		,,
14·82	14·82	70·36	75°	NH_4Cl
14·16	15·17	70·67		,,
13·11	15·79	71·10		,,
11·82	16·61	71·57		,,

Table XXVIII.—System NH_4Cl–HCl–H_2O *Between* 0° *and* −75°*C.*[5]

Molar percentage			Temperature, °C.	Solid Phase
NH_3	HCl	H_2O		
—	3·74	96·26	−9·6	ice
0·98	4·06	94·95	−10·4	”
1·41	4·21	94·68	−10·9	”
2·82	4·66	92·52	−11·8	”
4·15	5·11	90·74	−11·8	”
5·58	5·58	88·84	−12·1	”
—	6·29	93·71	−21·7	ice
1·80	6·07	92·13	−18·0	”
3·03	5·91	91·06	−16·1	”
4·52	5·72	89·76	−13·8	”
5·58	5·58	88·14	−12·8	”
—	12·6	87·84	−68·0	ice
5·58	5·58	88·84	−12·1	”
—	6·82	93·18	−24·6	ice
0·72	7·44	91·84	−25·2	”
1·18	7·84	90·98	−28·0	”
—	4·90	95·1	−14·0	ice
1·53	5·18	93·29	−19·2	”
0·39	11·69	87·92	−33·5	NH_4Cl
1·03	10·95	88·02	−13·8	”
2·28	9·48	88·24	−8·6	”
4·04	7·40	88·56	−12·5	”
4·69	6·63	88·64	−16·8	”
1·99	8·54	88·47	−19·6	NH_4Cl
3·39	9·82	82·83	−0·2	”
2·70	7·61	89·69	−15·1	NH_4Cl
4·10	8·82	87·08	−3·8	”
0·20	11·95	88·85	−18·6	ice + NH_4Cl
1·60	6·74	91·66	−20·3	”
1·18	7·78	91·04	−27·9	”
0·20	11·95	87·85	−75·0	”
0·1	13·5	86·4	−91 extrapolated	ice + NH_4Cl + $HCl,3H_2O$

NH_4Cl–$LiCl$–H_2O

Data relating to this system are scanty; they indicate that the two salts form no double compounds.[7]

NH_4Cl–$NaCl$–H_2O

Like the system NH_4Cl–NH_3–H_2O, this system is important in the manufacture of ammonium chloride and several workers have studied it with the results summarized in Table XXIX.[8–12] Above 0° solid phases are NaCl and NH_4Cl, whilst below 0° they are $NaCl,2H_2O$, NH_4Cl and ice. Mixed crystal formation has not been observed.

Table XXIX.—System NH_4Cl–$NaCl$–H_2O*—Compositions of Saturated Solutions —Weight Percentage*

−10°		0°		10°		25°		40°		60°		80°	
NH_4Cl	NaCl	NH_4Cl	NaCl	NH_4Cl	NaCl	NH_4Cl	NaCl	NH_4Cl	NaCl	NH_4Cl	NaCl	NH_4Cl	NaCl
0	24·3	0	26·3	0	26·3	0	26·4	0	26·7	0	27·0	0	27·5
5·5	21·4	10·2	19·9	12·5	18·3	15·9	17·1	19·4	15·5	24·4	15·7	29·5	12·0
8·7	19·7	15·3	11·1	25·0	0	21·5	8·9	31·4	0	29·2	7·4	39·6	0
15·4	8·0	22·9	0			28·3	0			35·6	0		
20·4													

NH_4Cl–KCl–H_2O

In this system, in contrast to the system NH_4Cl–$NaCl$–H_2O, mixed crystal formation does occur,[13] though not to give a continuous series of crystals since there appears to be a gap between 26·6 and 98·6 mol.-% NH_4Cl in the solid phase, as shown in Table XXX. This lack of continuity may account for one author having concluded that the single chlorides are the only solid phases.[14] Two types of mixed crystal are formed: face-centred cubes consisting of potassium chloride that has taken up ammonium chloride and body-centred cubes consisting of ammonium chloride with implanted potassium chloride.

Table XXX.—System NH_4Cl–KCl–H_2O *at 25°C.*[13]

Saturated solution at 25°			Solid phase	
mol.-% NH_4Cl	mol.-% KCl	mol.H_2O	mol.-% NH_4Cl	Crystal type
0	100	11·4	0	face-centred
7·9	92·1	10·0	3·0	,,
32·2	67·8	9·58	2·5	,,
52·4	47·6	8·47	9·2	,,
56·2	43·8	8·05	11·0	,,
68·5	31·5	7·13	19·4	,,
70·5	29·5	7·07	22·4	,,
73·3	26·7	6·89	26·6	,,
74·2	25·8	6·67	98·6	body-centred
76·1	23·9	6·78	98·5	,,
84·6	15·4	7·00	99·1	,,
100·0	0	7·5	100·0	,,

The solubility diagram shows two curves intersecting at a triple point corresponding to 25·8 mol.-% KCl, 74·2 mol.-% NH_4Cl, 6·67 mol. H_2O.

(*a*) NH_4Cl–NH_4Br–H_2O
(*b*) NH_4Cl–NH_4I–H_2O

In system (*a*), which has been studied at 25° as shown in Table XXXI, a continuous series of mixed crystals is formed[13] and the solubility curve is continuous, though it shows a flat minimum at the approximate composition of 55·0 mol.-% NH_4Br, 45 mol.-% NH_4Cl, 5·90 mol. H_2O. At this point solution and mixed crystal have the same composition.

In system (*b*), which has been studied at 20°, it has been reported that no mixed crystals are formed.[15] The solubility of each salt is depressed by the other, resulting in a ternary eutectic having a composition (by weight) of 7·30% NH_4Cl, 56·10% NH_4I, 36·6% H_2O. An equation has been derived showing the effect of ammonium iodide on the solubility of ammonium chloride from 0% of NH_4I to the eutectic composition:

$$x_1 = 28{\cdot}07-0{\cdot}4292x_2+0{\cdot}001015x_2^2$$

where x_1 is the wt.-% of NH_4Cl and x_2 the wt.-% of NH_4I in the saturated solution. The same author has also studied the system NH_4Cl–NH_4Br–NH_4I–H_2O.[16]

Table XXXI.—System NH_4Cl–NH_4Br–H_2O *at 25°C.*[13]

Saturated solution at 25°			Solid phase
mol.-% NH_4Cl	mol.-% NH_4Br	mol. H_2O	mol.-% NH_4Br
100·0	0	7·47	0
83·8	16·2	6·92	3·8
75·1	24·9	6·64	6·2
65·5	34·5	6·38	11·0
57·7	42·3	6·12	17·2
51·7	48·3	5·89	33·2
45·7	54·3	5·91	52·7
40·2	59·8	5·95	72·0
37·0	63·0	5·94	75·6
21·8	78·2	6·30	90·7
0	100·0	6·92	100·0

$(NH_4,K,Rb)Cl$–H_2O

This system has been studied at 25° as an example of equilibria of isomorphous salts in the solid phase formed from saturated solution of three salts having a common ion and forming reciprocal salt pairs.[17]

NH_4Cl–NH_4NO_3–H_2O

According to some workers no solid solutions, complex salts or hydrates are formed in this system at temperatures between 0·4° and 50°.[18] On the other hand, in somewhat earlier investigations a leading authority in the field observed that over the range 0–100° ammonium nitrate crystallized with from approximately 2 to 4 mol.-% of ammonium chloride.[19] The system has also been investigated below freezing point and a triple point found to lie at $-22°$ corresponding to 11·4% NH_4Cl, 27·0% NH_4NO_3 and 61·1% H_2O.[20] Typical data are given in Tables XXXII and XXXIII. The salting out action of ammonium nitrate appears to increase with temperature from $-20°$.

Table XXXII.—System NH_4Cl–NH_4NO_3–H_2O*—Compositions of Saturated Solutions*

NH_4Cl	NH_4NO_3	Temperature	Reference
% by wt. 11·2	33·8	−15°	22
11·0	37·7	−10°	22
10·4	44·6	0·4°	18
9·36	60·4	25°	18
9·24	70·8	50°	18

Table XXXIII.—System NH_4Cl–NH_4NO_3–H_2O *at 25°C.*[18]

NH_4Cl	NH_4NO_3	Solid phase
% by wt. 0·0	67·7	NH_4NO_3
2·00	66·3	,,
3·82	64·7	,,
5·58	62·2	,,
6·97	61·7	,,
9·36	60·4	$NH_4NO_3+NH_4Cl$
11·1	53·5	NH_4Cl
13·6	44·5	,,
15·8	37·0	,,
18·2	29·6	,,
21·8	19·0	,,
25·2	6·14	,,
28·3	0·0	,,

NH_4Cl–KNO_3–H_2O

This system, which is of some importance in certain European countries in relation to methods of making potassium nitrate for use as a fertilizer from naturally occurring potassium chloride and synthetic ammonium nitrate, has as a result received a good deal of attention and data are available from −20° to 100°.[19, 21–24] Boiling points of concentrated solutions in the system have also been studied.[25]

The system has also been investigated in the presence of ammonia from −10° to 40°.[26] At constant ammonia concentration a rise in temperature brings about an increase in the mutual solubility of ammonium chloride and ammonium nitrate, whilst at constant temperature the solubility increases with an increase in the concentration of ammonia.

More complicated related systems have been investigated, for example the biternary system of five components (NH_4, Na, K, Cl, NO_3)–H_2O underlying the conversion of sylvite into sodium nitrate and potassium nitrate.[27]

NH_4Cl–$(NH_4)_2SO_4$–H_2O

As shown in Table XXXIV this system has been investigated by one worker at 0°, 25°, 40°, 60°, 80°, during a study of the quaternary system NH_4Cl–Na_2SO_4–$(NH_4)_2SO_4$–NaCl–H_2O [9]; others have investigated it as a separate system at 20° and 30°.[28, 29] None of these workers has observed any formation of mixed crystals.

Table XXXIV.—System NH_4Cl–$(NH_4)_2SO_4$–H_2O *between* 0° *and* 80°*C.*

% by wt. NH_4Cl	$(NH_4)_2SO_4$	Solid phase	°C.	Reference
39·6	0	NH_4Cl	80°	9
27·4	23·2	NH_4Cl, $(NH_4)_2SO_4$	,,	,,
0	48·8	$(NH_4)_2SO_4$	,,	,,
35·6	0	NH_4Cl	60°	,,
29·5	11·6	,,	,,	,,
23·6	25·8	NH_4Cl, $(NH_4)_2SO_4$	,,	,,
0	46·8	$(NH_4)_2SO_4$	,,	,,
31·4	0	NH_4Cl	40°	,,
19·4	24·8	NH_4Cl, $(NH_4)_2SO_4$	,,	,,
0	44·8	$(NH_4)_2SO_4$	,,	,,
29·3	0	NH_4Cl	30°	29
25·0	6·6	,,	,,	,,
21·7	12·8	,,	,,	,,
19·8	19·6	,,	,,	,,
17·9	25·3	NH_4Cl, $(NH_4)_2SO_4$	,,	,,
16·6	26·3	$(NH_4)_2SO_4$	,,	,,
10·9	31·5	,,	,,	,,
0	42·7	,,	,,	,,
22·9	0	NH_4Cl	0°	9
17·1	13·9	,,	,,	,,
11·3	28·4	NH_4Cl, $(NH_4)_2SO_4$	,,	,,
0	41·1	$(NH_4)_2SO_4$	,,	,,

The reciprocal salt pair $(NH_4)_2SO_4 + 2KCl \rightleftharpoons K_2SO_4 + 2NH_4Cl$ has been studied in water and also in water and ammonia at 25° [30] as a background to a process for making potassium sulphate from polyhalite by using the reaction between ammonium sulphate and potassium chloride in an aqueous solution saturated with ammonia. Three solid phases exist: (i) NH_4Cl containing up to 2·5% KCl; (ii) KCl containing up to 16·6% NH_4Cl; and (iii) K_2SO_4 and $(NH_4)_2SO_4$ in all ratios.

(*a*) NH_4Cl–$NH_4H_2PO_4$–H_2O
(*b*) NH_4Cl–Na(K)H_2PO_4–H_2O

Studies of these systems have provided data for devising processes for making various phosphate-containing fertilizers. System (*a*) has been investigated at 0° with the results shown in Table XXXV,[31] and also between −15·6° and 30°,[32] and at 25°.[33] It forms a ternary eutectic at −15·6° having the composition NH_4Cl 17·8%, $NH_4H_2PO_4$ 3·9% and H_2O 78·3% by weight.

Table XXXV.—System NH_4Cl–$(NH_4)H_2PO_4$–H_2O *at* 0°*C.*[31]

Mol.-%		Mols. H_2O	Solid phases
NH_4Cl	$NH_4H_2PO_4$		
100·0	0	10·0	NH_4Cl
98·3	1·7	9·9	,,
92·2	7·8	9·5	NH_4Cl–$NH_4H_2PO_4$
78·6	21·4	14·9	$NH_4H_2PO_4$
62·9	37·1	20·6	,,
44·6	55·4	22·7	,,
20·2	79·8	24·5	,,
0	100·0	28·1	,,

System (*b*) has been investigated at 0° and 25° with sodium monophosphate,[34] and at 25° with potassium monophosphate.[33] The phase diagrams in the latter showed that a mixed phosphatic fertilizer $m$$KH_2PO_4$,$n$$NH_4H_2PO_4$ could be readily made by passing ammonia into a mixture of technical orthophosphoric acid and potassium chloride, separating the solid phase by centrifuging and saturating the mother liquor with ammonia to recover further solids. In this way 98–99% of the P_2O_5 is utilized.

NH_4Cl–$MgCl_2$–H_2O

This system has been studied at temperatures between 115° and −34·6°, the eutectic point.[35] No solid solutions were detected but fields corresponding to hydrates of $MgCl_2$, of NH_4Cl, to NH_4Cl,$MgCl_2$,$6H_2O$ and to ice were observed. Ammonium chloride is only very slightly soluble in saturated solutions of magnesium chloride. The hydrated double salt NH_4Cl,$MgCl_2$,$6H_2O$ is formed above −32° and dissolves incongruently up to 50°. Tensimetric studies of NH_4Cl,$MgCl_2$,$6H_2O$ and the various hydrates of $MgCl_2$ show that the presence of NH_4Cl in the molecule weakens the bond between salt and water. For example over phosphorus pentoxide $MgCl_2$,$6H_2O$ dehydrates only to $MgCl_2$,$4H_2O$, whereas NH_4Cl,$MgCl_2$,$6H_2O$ proceeds readily to NH_4Cl,$MgCl_2$,$2H_2O$ and beyond.

NH_4Cl–$ZnCl_2$–H_2O

This system, particularly in the presence of ammonia, has some bearing on the chemical process underlying the operation of the Leclanché type of cell especially in its form of the ordinary dry battery, since in an undischarged dry battery the electrolyte consists mainly of zinc chloride, ammonium chloride and water. One study[36] has shown that at 21° saturated solutions containing up to 25% of zinc chloride are in equilibrium with solid ammonium chloride, those containing 25% to 41·4% of zinc chloride are in equilibrium with $ZnCl_2$,$3NH_4Cl$, and those above 41·4% in equilibrium with $ZnCl_2$,$2NH_4Cl$. These findings correspond to practical experience in dry battery manufacture showing that electrolytes containing 25% to 41·4% of zinc chloride are unsatisfactory because they permit the growth of crystals resulting in high internal resistance in and mechanical disintegration of the depolarizer. The addition of ammonia to the system at 20° precipitates $ZnCl_2$,$2NH_3$

when the ammonium chloride content is about 15% or above, and a basic zinc chloride, probably $ZnCl_2,4ZnO$, when the ammonium chloride content is less than 15%.[37] During normal discharge of dry batteries $ZnCl_2,2NH_3$ is produced at the cathode, but on heavy discharge it appears that $ZnCl_2,4NH_3$ is formed.

NH_4Cl–$HgCl_2$–H_2O

This system has been studied in a limited way to obtain information about complexes of the two salts.[38, 39] At 25–30° some three to seven complexes may be formed depending on the concentrations of the salts. Mercuric cyanide forms in solution the double salt $NH_4Cl,Hg(CN)_2$.[40] The more complicated related system NH_4Cl–KCl–$HgCl_2$–H_2O was investigated[41] along with other similar systems in which isomorphous salts appear as solid phases from saturated solutions of three salts having a common ion and reciprocal salt pairs.

NH_4Cl–$PbCl_2$–H_2O

This system was studied at 25°, as shown in Table XXXVI, as part of an investigation of equilibria in aqueous solutions as lead chloride.[42] Earlier work had shown the existence of $NH_4Cl,2PbCl_2$ and $PbCl_2,2NH_4Cl$ at 100°, the latter being stable only above 75°, and the former stable down to room temperature.[43]

Table XXXVI.—System NH_4Cl–$PbCl_2$–H_2O *at 25°C.*[42]

Saturated solutions		Solid phase
g. $PbCl_2$/1000 g. H_2O	g. NH_4Cl/1000 g. H_2O	
10·91	—	$PbCl_2$
3·04	9·62	,,
2·00	22·3	,,
1·76	34·2	,,
1·44	43·0	$PbCl_2+NH_4Cl,2PbCl_2$
1·45	44·2	,,
1·35	48·0	$NH_4Cl,2PbCl_2$
1·21	65·6	,,
1·22	86·1	,,
1·21	102·1	,,
1·57	146·5	,,
4·58	270·0	,,
13·63	394·5	,,
14·46	403·3	$NH_4Cl,2PbCl_2+NH_4Cl$
10·42	403·9	NH_4Cl
7·28	401·1	,,
5·40	400·6	,,
—	397·8	,,

It may be seen from Table XXXVI that the transition point at which both the solid phases $PbCl_2$ and $NH_4Cl,2PbCl_2$ are in stable equilibrium occurs at a lower NH_4Cl concentration than that which gives the minimum solubility of $PbCl_2$.

(*a*) NH_4Cl–$CuCl$–H_2O
(*b*) NH_4Cl–$CuCl$–HCl–H_2O

A study of system (*a*) has shown[44] that at 25° $NH_4Cl,2CuCl$ exists, at 50° $NH_4Cl,CuCl$, whilst by 80° double salt formation has ceased. In system (*b*) which the same worker investigated at 50°, 80° and 100°, the double salt $NH_4Cl,CuCl$ was found to be present only at 50°; increasing temperature causes an increase in the area of the HCl field and a decrease in that of the NH_4Cl. At 100° the salting-out effect of HCl on NH_4Cl is very slight.

$NH_4Cl–CuCl_2–H_2O$

An investigation of this system at 0° and 25° has shown that the compound $2NH_4Cl,CuCl_2,2H_2O$, which for long was regarded as a double salt, is really a mixed crystal or solid solution.[45]

$NH_4Cl–CuCl_2–HCl–H_2O$

Phase diagrams for this quaternary system have been constructed from data for the related ternary systems, one of which is $NH_4Cl–CuCl_2–H_2O$, at 25° and 80°. A feature of the system is a large solid-solution field involving $CuCl_2,2NH_4Cl,2H_2O$ at 25° which still exists at 80°.[46] Some of the more important points in the diagram correspond to data given in Table XXXVII.

Table XXXVII.—System $NH_4Cl–CuCl_2–HCl–H_2O$ *at* 25° *and* 80°C.[46]

Temperature	% by wt.			Solutions saturated with respect to
	$CuCl_2$	NH_4Cl	HCl	
25°	43·0	2·0	—	$CuCl_2$
,,	1·82	26·9	—	NH_4Cl
,,	0·32	5·24	39·3	NH_4Cl,HCl
,,	26·8	0·74	28·9	$CuCl_2,HCl$
80°	50·5	8·2	—	Solid solution
,,	7·06	37·6	—	,,
,,	2·45	12·8	23·2	,,
,,	35·1	5·1	16·4	,,

$NH_4Cl–Na_2Cr_2O_7–H_2O$

Ammonium dichromate is usually prepared by the double decomposition:

$$Na_2Cr_2O_7 + 2NH_4Cl \rightleftharpoons (NH_4)_2Cr_2O_7 + 2NaCl$$

The large difference between the temperature coefficients of the solubilities of ammonium dichromate and sodium chloride makes it easy to separate the two salts by successive evaporations and crystallizations, and in this way ammonium dichromate can be obtained in very good yield. The system, or more accurately the reciprocal salt pair, was investigated at 0°, 20°, 50° and 75° in connection with this double decomposition and at the same time the related systems $(NH_4)_2Cr_2O_7–NH_4Cl–H_2O$, $(NH_4)_2Cr_2O_7–Na_2Cr_2O_7–H_2O$, $Na_2Cr_2O_7–NaCl–H_2O$ and $NH_4Cl–NaCl–H_2O$ were studied.[47]

$NH_4Cl–MnCl_2–H_2O$

Those who have worked on this system have found its main interest to lie in the many solid solutions that it contains, for it and the system $NH_4Cl–FeCl_3–H_2O$ are the typical anomalous solid-solution systems. In earlier work three sets of solid solutions were identified at 60°, among which the double salt $2NH_4Cl,MnCl_2,2H_2O$ occurred, and there were signposts pointing towards the extensive anomalous solid-solution fields located by later workers. Thus it was noted that the composition of the solid solution varied with the time it had been in contact with the liquid phase as if a kind of supersaturated solid solution were first formed which later cast off one of its constituents.[48] In a wider investigation[49] the same author showed that over the temperature range 10–70° there was a lower critical solution temperature just below 25°. Later work by others at 25° confirmed the existence of this double salt and disclosed four groups of anomalous solid solution systems in all of which dispersion media and dispersed phase possess definite crystal forms.[50] A mechanism for the formation of the anomalous solid solutions has been suggested and reasons advanced for the failure of Vegard's additivity law to apply to those solid solutions in which the components have dissimilar chemical and crystal structures.[51] Solid solutions of the $NH_4Cl–MnCl_2–H_2O$ system are said to exhibit properties characteristic of order–disorder in alloys[52]; for example the application of thermal and cold-working methods to the solid solution can produce the disordered from the ordered state as with alloys. Disordered solid solutions possess the same cubical crystal structure as does ammonium chloride, whereas ordered solid solutions exhibit the formation of superstructures and tetragonal symmetry and conform to a normal Vegard's law relation, i.e. that the unit cell dimensions in a continuous solid solution series vary linearly with the mole fraction of solute present. Experiments with radiomanganese in the system $NH_4Cl–MnCl_2–H_2O$ indicate a limiting concentration below which solid solutions of NH_4Cl and $MnCl_2$ cannot form. Such a limiting concentration is believed to prove that the solid solutions have a microdispersed structure instead of a molecularly dispersed one; they are thus 'solid colloidal solutions'.[53, 54]

(*a*) $NH_4Cl–FeCl_2–H_2O$
(*b*) $NH_4Cl–FeCl_3–H_2O$

Both of these systems, together with those analogous to system (*a*) containing $MnCl_2$, $CoCl_2$, or $NiCl_2$ instead of $FeCl_2$, were investigated as part of a general study of solid solution formation in ternary systems,[55, 56] but the full extent of the range of solid solutions was apparently not realized. Over twenty years later the existence in system (*a*) of two series of microdispersed solid solutions was demonstrated, the α-series being formed from solutions containing up to 26% $FeCl_2$ and the β-series from 26% to 40% of $FeCl_2$. At the eutectic point the solution contains 4·96% of NH_4Cl and 39·6% of $FeCl_2$ and is in equilibrium with the β-solid solution and with $FeCl_2,4H_2O$.[57] In system (*b*) the compounds $NH_4Cl,FeCl_3$ and $NH_4Cl,4FeCl_3,6H_2O$ separate out at 60°, but the existence of $2NH_4Cl,FeCl_3,H_2O$ postulated by Roozeboom for this system was not confirmed, and in addition the compound $NH_4Cl,2FeCl_3,4H_2O$ previously mentioned in the literature as appearing at 45° was shown to be theoretically impossible as a stable solid. Other data relating to system (*b*) have been discussed in general terms in connection with the formation of anomalous solid solutions.[58]

$NH_4Cl–CoCl_2–H_2O$

This system has been studied at 60°,[55] at 25° and 50°,[59] and at various temperatures between 0° and 100°.[60] At 60° there is a continuous series of solid solutions from NH_4Cl to $CoCl_2,2H_2O$. All workers agree now that the double salt $CoCl_2,2NH_4Cl,2H_2O$ exists, though on the basis of experiments twelve years earlier one of them[61] had then concluded that double salts of $CoCl_2$ and NH_4Cl did not occur in the solid form at any temperature. It appears also that microdispersed solid solutions are formed, those of α-type consisting of a true solid solution of $CoCl_2,2H_2O$ or $CoCl_2,2NH_4Cl,2H_2O$ in NH_4Cl with the double salt distributed through the crystals also in a state of microdispersion, and those of β-type consisting of a solid solution of the double salt in NH_4Cl with $CoCl_2,2H_2O$ in a state of microdispersion.

The same system containing added ammonia has been examined calorimetrically.[62, 63]

$NH_4Cl–NiCl_2–H_2O$

This system has been studied at 0°, 25° and 50°[64, 65] and appears to offer further examples of microdispersed solid solutions similar to those formed by ammonium chloride with other transition metal chlorides.[66–70] The solid solutions consist of two components, $NH_4Cl,NiCl_2,2H_2O$ and NH_4Cl; one series consists of the former as the dispersion medium and the latter as the dispersed phase, in the other series the rôles are reversed.

Miscellaneous Systems

There are references in the literature to several systems not readily classifiable in any of the foregoing groups. Among these are the following:

- (*a*) $NH_4Cl–Na_2B_4O_7–H_2O$[71]
- (*b*) $NH_4Cl–(NH_4)_2CO_3–NaCl–Na_2CO_3–H_2O$[72]
- (*c*) $NH_4Cl–NH_4HCO_3–NaCl–NaHCO_3–H_2O$
    - (i) at normal pressure[73–75]
    - (ii) at pressures up to 70 atm.[76, 77]
- (*d*) $NH_4Cl–(NH_4)_4Fe(CN)_6–H_2O$[78]
- (*e*) $NH_4Cl–NH_4F–(NH_4)_2SiF_6–H_2O$[79]
- (*f*) $NH_4Cl–NH_4SO_3NH_2–H_2O$[80]

System (*a*) is of interest in the extraction of borax; (*b*) in the manufacture of ammonium chloride in the ammonia–soda process; (*c*) in the ammonia–soda process, particularly at elevated pressure under which the customary 75% usage of NaCl in ammonia–soda plants working at normal pressures can be increased to over 85%. System (*d*) has Bunsen's salt $(NH_4)_4Fe(CN)_6,2NH_4Cl$ as one of the solid phases, and no evidence was found for its existence in a hydrated form or for the presence of covalent bonds between iron and chlorine atoms.

Included among other data on miscellaneous solubility relationships not extensive enough to rank as systems, are solubilities in ammonium chloride solutions of calcium oxalate at 30°, 37°, 50° and 95°[81, 82]; of calcium sulphate[83] and of boric acid over the range 0–100°[84, 85]; of sodium chloride in mixed solutions of ammonium chloride and calcium chloride, and of barium chloride in mixed solutions of ammonium chloride and sodium chloride.[86]

NON-AQUEOUS SYSTEMS CONTAINING AMMONIUM CHLORIDE

Liquid Ammonia

Ammonium chloride dissolves in liquid ammonia to form various ammonium ammino-chlorides, but above about 36° the solid phase in equilibrium with the solution is NH_4Cl which is bimolecularly associated.[87, 88] The heat of solution at $-33{\cdot}4°$ is 6·4 kcal./mol.[89] Various workers have determined the solubility at different temperatures and typical data are given in Table XXXVIII.[90–96]

Table XXXVIII.—Solubilities of Ammonium Chloride in Liquid Ammonia[98]

Temperature, °C.	% NH_4Cl	Solid phase
−52·9	5·23	$NH_4Cl,3NH_3$
−39·3	10·0	,,
−20·5	22·6	,,
−11·8	29·5	,,
0·9	40·6	,,
4·2	44·2	,,
8·2	49·2	,,
9·1	50·5	,,
9·8	51·5	,,
9·3	52·5	,,
8·3	54·0	,,
36·9	55·4	NH_4Cl

Densities, given in Table XXXIX, and vapour pressures of solutions of ammonium chloride in liquid ammonia, given in Table XL, have been determined,[97–99] as well as viscosity coefficients[100] and decomposition pressures of ammino-chlorides.[101]

Table XXXIX.—Densities of Liquid Ammonia Solutions of Ammonium Chloride[97]

g. NH_4Cl/100 g. NH_3	Density of solution at 15°
0	0·618
4·06	0·641
20·8	0·719

Table XL.—Vapour Pressures of Liquid Ammonia Solutions of Ammonium Chloride at 25°C.[99]

Mols. NH_3/mol. NH_4Cl	Vapour pressure
2·06	314·0 cm. Hg
4·32	595·8
6·71	685·6
8·55	707·0
12·2	722·3
16·0	729·0
20·0	732·4
32·0	737·6
51·3	741·7
60·7	742·5
86·4	744·2
105	745·2
122	745·9
143	747·1

The specific conductivity of the saturated solution is $3{\cdot}3 \times 10^{-3}$ mhos at −65°, and the equivalent conductivity at infinite dilution 335 mhos at −50.° [90] There are other references to electrical conductivities.[102, 103] Activity coefficients, given in Table XLI, have been determined by several workers, in some cases by means of electromotive force measurements, in others through vapour pressure lowering.[104–106] Agreement with values for the coefficients calculated by means of the Debye–Hückel theory is satisfactory only at very low molalities even after applying partial dissociation corrections.

Table XLI.—Activity Coefficients of Ammonium Chloride in Liquid Ammonia Solutions at 25°C.[106]

Molality of NH_4Cl	Activity coefficient at 25°
0·0025	0·653
0·0225	0·341
0·040	0·275
0·160	0·139
1·00	0·0344
4·00	0·0111
10·7	0·00604
16·3	0·00608
18·9	0·00659
21·8	0·00732
24·4	0·00822

Electrolysis of solutions of ammonium chloride in liquid ammonia exhibits nitrogen-overvoltage phenomena.[107] Heats of reaction of metallic lithium, sodium, potassium and cæsium with dilute solutions of ammonium chloride in liquid ammonia all lie between 39·7 and 41·6 kcal./mol. indicating a close similarity in the nature of dilute solutions of the alkali metals in liquid ammonia.[108]

Liquid Sulphur Dioxide

In the older literature ammonium chloride was described as insoluble in liquid sulphur dioxide, but from more recent work[109] it appears that though its solubility is small it is in fact measurable, amounting to 0·0031% by weight at 25°.

Methyl Alcohol

The solubility of ammonium chloride in methyl alcohol given in Table XLII[110] and in methyl alcohol/water mixtures exemplified in Table XLIII,[111–113] and also the densities and viscosities of solutions have been measured mainly in attempts to test the various theories of solutions of electrolytes usually associated with Debye, Hückel, Onsager and Fuoss.

Table XLII.—Solubilities of Ammonium Chloride in Methyl Alcohol[110]

Temperature, °C.	g. NH_4Cl/100 g. MeOH in saturated solution
25	3·61
35	3·89
45	4·15
55	4·46

Table XLIII.—Solubilities of Ammonium Chloride in Methyl Alcohol/Water Mixtures at 25°C.[113]

MeOH/H_2O mixtures at 25°		
% MeOH	g. NH_4Cl/100 g. solvent	Density of saturated solution
0	39·3	1·078
10	35·5	1·047
30	27·7	1·027
50	20·2	0·984
70	11·3	0·910
80	8·12	0·876
90	5·48	0·850
100	3·61	0·805

Conductivities and densities have also been determined in the system NH_4Cl–$ZnCl_2$–MeOH from −50° to 20°,[114] and extensive complex formation has been observed.

Ethyl Alcohol

Solubilities of ammonium chloride in ethyl alcohol/water mixtures have been determined for use in purifying the salt from traces of ferric chloride by fractional crystallization,[115] and in determining vapour–liquid equilibria of EtOH/H_2O systems.[116] The following empirical equations have been given[113] for y, the solubility in g./100 g. of mixed solvent:

$$y = 37{\cdot}4 - 0{\cdot}397x \qquad \text{for } x = 0 \text{ to } 80 \text{ vol.\% EtOH}$$

and

$$165{\cdot}1y = (110{\cdot}71 - x)^2 \qquad \text{for } x = 80 \text{ to } 100 \text{ vol.\%}$$

Conductivities of solutions in ethyl alcohol/water mixtures have been measured as in the case of methyl alcohol/water mixtures in connection with theories of strong electrolytes. The equivalent conductivity in 100% ethyl alcohol at infinite dilution has been given as 43·0 mhos, and the dissociation constant as 0·0167.[117]

Butyl Alcohol

The system *tert.*-butyl alcohol–NH_4Cl–H_2O illustrated in Table XLIV has been studied at 30° as part of an investigation into the effects of various halides, sulphates and carbonates as salting out agents.[118]

Table XLIV.—Solubilities of Ammonium Chloride in Aqueous Tertiary Butyl Alcohol[118]

% *tert.*-butyl alcohol by wt.	% NH_4Cl by wt. in saturated solution
7·6	24·7
10·2	18·4
20·7	9·4
30·2	6·6
39·3	5·0
61·2	3·3
82·0	2·0

Acetone

In acetone ammonium chloride is practically insoluble, in contrast to the bromide and iodide both of which possess measurable solubilities.[119]

Acetic Acid

Data are available, as shown in Tables XLV and XLVI, for the solubility of ammonium chloride in anhydrous acetic acid between 15° and 100° [120] and for conductivities of dilute solutions at 25°.[121]

Table XLV.—Solubilities of Ammonium Chloride in Acetic Acid.[120]

mol. % NH_4Cl in saturated solution	Temperature, °C.
0·053	21
0·084	32
0·110	43
0·134	53
0·178	65
0·224	77
0·282	87
0·348	98

Table XLVI.—Electrical Conductivities of Acetic Acid Solutions of Ammonium Chloride at 25°C.[121]

mols. NH_4Cl/litre	Equivalent conductivity in mhos
0·00257	0·2241
0·000979	0·34
0·000290	0·599
0·0000979	0·984
0·0000555	1·28
0·0000188	2·10

Hydrogen Cyanide

Ammonium chloride is sparingly soluble in anhydrous liquid hydrogen cyanide. The equivalent conductivity at infinite dilution is 383·3 mhos at 18°, and the equivalent conductivity–concentration curves agree well with the Debye–Hückel–Onsager equations.[122]

Phosphorus oxychloride

The solubility of ammonium chloride in anhydrous phosphorus oxychloride at 20° is 0·46 g./l. and the specific conductivity of the saturated solution is $3{\cdot}6 \times 10^{-5}$ mhos. In comparison with tetramethylammonium chloride, which is moderately dissociated in the solution, ammonium chloride like the alkali metal halides is only slightly dissociated.[123]

Miscellaneous Solvents

In formamide and dimethylformamide determinations respectively of f.p.[124] and conductivities[125] have been made for the purpose of testing modern theories of solutions; conductivities of mixtures of ammonium chloride and aluminium bromide have been measured in xylene[126] and in nitrobenzene[127, 128]; solubilities of aniline in ammonium chloride solutions have been found to be not inappreciable, for example a 3% solution dissolves 3·37% of aniline.[129] In molten iodine monochloride at 55° conductometric titrations of ammonium chloride against stannic chloride have shown that the former behaves as a base and neutralizes the latter.[130] It appears that the reaction proceeds by formation of ionized compounds with the iodine monochloride which in turn react to give the neutral salts.

FUSED SYSTEMS CONTAINING AMMONIUM CHLORIDE

NH_4Cl–MCl_x (M = Li,Cu,Zn,Cd,Fe^{3+})

Systems composed of ammonium chloride and other less volatile chlorides are unusual in that, since one component sublimes without melting, the b.p. curves intersect the m.p. curves. In his classic work on the phase rule Roozeboom gave diagrams for various binary systems unknown at the time, and it was not until many years later that examples of some of these were found among the systems NH_4Cl–$CuCl$, NH_4Cl–$LiCl$, NH_4Cl–$ZnCl_2$, NH_4Cl–$CdCl_2$ and NH_4Cl–$FeCl_3$.[131–133] In general these systems resemble ordinary binary systems until mixtures rich in ammonium chloride are reached. They are invariant at the temperature of intersection of the melting point and boiling point curves, where a boiling liquid co-exists with solid ammonium chloride and a saturated vapour containing only a small amount of the metal chloride. Compounds of NH_4Cl with $CuCl$ and NH_4Cl with $LiCl$ were not observed, but $NH_4Cl,2ZnCl_2$, $NH_4Cl,CdCl_2$, $NH_4Cl,2CdCl_2$ and $NH_4Cl,FeCl_3$ were identified.

NH_4Cl–NH_4NO_3

In a study of the reciprocal salt pair NH_4NO_3–$NaCl$ one investigator concluded that ammonium chloride and ammonium nitrate do not form double salts or isomorphous mixtures,[134, 135] but later another worker,[136] though confirming the position of the liquidus curves and the eutectic determined by the first investigator, discovered a series of solid solutions. In this series all mixtures exist from pure NH_4NO_3 to (92% of NH_4NO_3 + 8% of NH_4Cl). One consequence of the existence of this series of solid solutions is that not until after the limits of solid solution are passed can the eutectic be formed (141°, 12·1% NH_4Cl, 87·9% NH_4NO_3).

NH_4Cl–NH_4Br

This system shows a complete series of solid solutions from pure ammonium chloride to pure ammonium bromide; the curve of melting points determined in sealed tubes shows a minimum at approximately 511° corresponding to about 65 mol.% NH_4Cl.

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NH_4Cl–$HgCl_2$

This system has been studied by determining electrical conductivities and melting points of mixtures of the two salts.[137–139] Incongruent melting points lie at 235° (23·5 mol.-% NH_4Cl), 214° (33·5%) and 243° (66·6%), corresponding respectively to the compounds 9 $HgCl_2$,2NH_4Cl, 2$HgCl_2$,NH_4Cl and $HgCl_2$,4NH_4Cl. Minima in plots of electrical conductivity against concentration, and of temperature-coefficient of conductivity against concentration, correspond to compound-formation and are very sharp in the system NH_4Cl–$HgCl_2$. There is also a compound $HgCl_2$,NH_4Cl melting congruently at 218°.

NH_4Cl–$NH_4H_2PO_4$

This system has a eutectic point at 184°, the solid containing 12·2 mol.-% of NH_4Cl. The related ternary system NH_4Cl–NH_4NO_3–$NH_4H_2PO_4$ has a eutectic point at 131·5°, corresponding to a composition of NH_4Cl 14, NH_4NO_3 80·2, and $NH_4H_2PO_4$ 5·8 mol.-%.[140]

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AMMONIUM CHLORIDE AEROSOLS

Preparation of Mists and Smokes

Ammonium chloride can exist in generally stable disperse phases in air, either as mists consisting of suspensions of droplets of solution or as smokes consisting of very fine particles of the solid. A method of making a mist is to pass one stream of air through concentrated aqueous ammonia, and another through concentrated hydrochloric acid, then to mix the two streams over water and finally to bubble the mist which is formed through water to remove any excess of either ammonia or hydrogen chloride.[1] Mists are also formed when air containing hydrogen chloride is passed through sodium hydroxide solution containing a trace of ammonia, or when air containing ammonia is passed through hydrochloric acid.[2] For a constant ammonia content the amount of fog passes through a maximum as the sodium hydroxide content increases until with a 50% solution containing 0·001% ammonia no fog is produced.

Ammonium chloride smokes may be made by drying a mist with phosphorus pentoxide, by heating very dry solid ammonium chloride in a stream of thoroughly dry air and by reacting dry ammonia and dry hydrogen in a closed space. In the last method a curious phenomenon of rhythmic precipitation is observed when the reactants are allowed to diffuse towards one another from opposite ends of a tube.[3]

The particle size in both mists and smokes is of the order of 10^{-5} to 10^{-4} cm. and in dry smokes the particles appear to be uncharged, at any rate initially, since they have been reported to give negative results on examination by means of electrometers and strong electric fields.[4] On the other hand there is reliable evidence that the particles gradually acquire charges from ions normally present in the atmosphere and the aerosol may as a result become more stable.[5] Acquisition of charges in this way may account for observations that the filtering capacity of certain mechanical barriers such as glass wool, pumice and rayon is related to the formation of electrically active points in the filtering mass,[6] and that the theoretically calculated rate of increase in the number of charged particles in initially uncharged or lightly charged aerosols agrees with experimental observations.[7]

Stability

The stability of ammonium chloride smokes is increased by some substances, for example phenol, *iso*amyl alcohol and octyl alcohol, and there appears to be an optimum concentration for each. The effect of water vapour is disputed, some workers maintaining that the smoke cannot be formed in absolutely dry air. There appears, however, to be a fair measure of agreement that, at the low concentrations resulting from a relative humidity of less than about 50% at room temperature, water vapour acts as a stabilizer, but that with increasing concentration it may cause coagulation. Butyric acid is said to coagulate the smokes, whilst oleic acid and methyl and ethyl alcohols have little effect. Methyl alcohol has been found to stabilize mists and carbon tetrachloride to coagulate them. The action of the stabilizer probably consists in surrounding the dispersed particles with an envelope of oriented molecules.[8–18] High-frequency sound coagulates ammonium chloride smokes, the rate of coagulation increasing rapidly with intensity and being more rapid the denser the smoke.[19] Several workers have studied the ageing of ammonium chloride smokes and the

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effect of air turbulence; in general, below a critical degree of turbulence the rate of coagulation is unaffected.[20–26]

Absorption

Both mists and smokes of ammonium chloride are absorbed in different degrees by such materials as active charcoal, fused calcium chloride, pumice, glass wool and filter paper. The granular barriers are less effective with mists than with smokes, the latter being more readily absorbed by materials possessing specific adsorptive capacity for gases. Various experimental investigations suggest that the low intrinsic mobility of the larger particles comprising mists results in low frequency of collision with the barrier, and hence reduces the chance of capture, whereas the smaller particles in smokes, having higher mobility, collide and are captured more frequently. Closely packed fibrous materials, such as glass-wool, filter paper and asbestos, possess the highest absorptive powers for both mists and smokes with efficiencies of between 50 and 90%, but these too are more effective in stopping smokes than mists. Liquids absorb mists and smokes to varying extents; thus it is possible to blow them once-through in water with less than 20% absorption, though over 75% may be achieved in multiple absorbers. Solutions of potassium hydroxide can absorb as little as 12% of mists and 70–80% of smokes.[27–32]

Optical Properties

Ammonium chloride smokes show maximum light transmission at a wave-length of 4580 A., whilst mists show a sharp maximum at 4400 A., and in general the mists are more transparent for the longer wave-lengths because of light scattering by the water particles.[33] The scattering of light by ammonium chloride smokes has been found to be almost independent of the wave-length.[34] The diffused reflective power of mists in the presence of carbon dioxide for sunlight incident at angles of 30–60° increases with the concentration of particles until with very dense mists the reflective power is nearly equal to that of a gypsum plate.[35] Ammonium chloride smokes exhibit birefringence and dichromatism in electric fields and there is experimental evidence that the birefringence is approximately inversely proportional to the square of the wave-length of the light, whilst the dichromatism is inversely proportional to its cube.[36] Ammonium chloride smokes occasionally exhibit stratification.[37]

An interesting use of ammonium chloride aerosols is in making carbon black by the channel process from natural gas. The yield may be increased by up to 45% by introducing into the natural gas an aerosol of a liquid hydrocarbon supported on nuclei of ammonium chloride.[38]

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CHEMICAL PROPERTIES OF AMMONIUM CHLORIDE

Ammonium chloride is stable in dry air but in contact with the atmosphere is very weakly hygroscopic, much less so than lithium and sodium chlorides, though slightly more so than potassium chloride. A combination of hygroscopicity, even though weak, and a tendency towards plastic flow causes ammonium chloride to cake, particularly during storage in bags and kegs. This can be prevented by uniformly mixing with the ammonium chloride very small proportions of additives of various kinds. Examples are: substances such as calcium hydroxyphosphate that act as a sponge for water and thus prevent the formation of cementing films of saturated solution round the individual ammonium chloride crystals; or substances such as certain dyes, notably acid magenta, and long-chain amine salts, for example octadecylamine acetate, that influence crystallization from the films of saturated solution either by preventing it entirely or by changing the crystal habit in such a way that only weak crystal bonds are formed between adjacent crystals. Additives having waterproofing action such as paraffin wax or stearic acid may also be used.[1–3]

Thermal Dissociation

When heated, ammonium chloride sublimes without melting, and the vapour is completely dissociated into hydrogen chloride and ammonia. It is remarkable that not until the beginning of the second quarter of the twentieth century was this apparently simple property fully recognized. When Mellor wrote about ammonium chloride (II, 565) there was still much disagreement about the interpretation of the results of experiments to determine the vapour density. Early workers of what might be called the classical period of H. B. Baker had maintained, on the basis of vapour density measurements by the methods of V. Meyer and Dumas, that intensively dried ammonium chloride vaporized without any dissociation taking place, but a little later other work had indicated degrees of dissociation of the order of 65% between 280° and 330°. Even as recently as 1927 measurement by means of a densi-tensimeter had led one investigator to deduce that not only were there completely undissociated molecules in the vapour but that below 286° there was partial

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association.[4, 5] These last results were shown, however, to be inaccurate by investigators who found that the saturated as well as the unsaturated vapour is completely dissociated within a temperature range of 250–390° under pressures of from 16 to 820 mm. Hg.[6]

Since it was known experimentally that the vapours of dry ammonium chloride and moist ammonium chloride exert the same pressure, the belief that the dry was undissociated and the moist dissociated was very difficult to explain. For there must be an equilibrium in the vapour phase between dissociated and undissociated molecules of ammonium chloride if both species exist, and in turn between each of these and solid ammonium chloride. On the old view, therefore, the removal of the last traces of water from the solid must shift this equilibrium, and the most probable way in which this could be imagined to come about would be for the removal of the last trace of moisture to increase the free energy of the solid and also prevent the establishment of the dissociation equilibrium. This supposition, though contrary to experience, is not thermodynamically impossible since the removal of traces of moisture might conceivably involve large energy changes, but it is so surprising that later workers were led to redetermine the vapour pressure and vapour density of ammonium chloride in various states of dryness. As a result the matter has been clarified[7, 8] by showing that the methods of V. Meyer and of Dumas for determining vapour density are inapplicable to ammonium chloride because, owing to its very low rate of vaporization when intensively dried, equilibrium is reached extremely slowly. For similar reasons results obtained from measurements of diffusion are unreliable. These experimental difficulties were resolved, however, by determining vapour density using microbalance methods to measure the buoyancy effect of the vapour on thin-walled tubes; in this way it was shown that at 315–325° using ammonium chloride dried for 10 days at 60° in high vacuum the dry vapour is completely dissociated. These findings have been confirmed in several ways; for example, values for the standard free energy of dissociation of ammonium chloride into ammonia and hydrogen chloride calculated by two independent paths are in good agreement,[9] and measurements of the dissociation pressure of ammonium chloride in equilibrium with excess of ammonia and hydrogen chloride in the vapour phase are in good agreement with the law of mass action.

The rates of evaporation and condensation of solid dried ammonium chloride are so very slow that the salt scarcely seems volatile at all. This behaviour is probably responsible for the reports in the older literature that gaseous ammonia and hydrogen chloride do not react when intensively dried. Even in vacuo the rate of vaporization of ammonium chloride has been found to be much less than is to be expected from its vapour pressure.[10] In the vapour-pressure equilibrium conditions the rate of vaporization from a layer of the solid is proportional to a higher concentration of loosely-bound ammonia and hydrogen chloride molecules. In vacuo the slowest step, which is rate-determining, is the transfer of ammonium chloride ion pairs from the crystal lattice to the surface. Another piece of evidence that the interconversion of solid and vapour is a chemical reaction rather than an unchanged sublimation is found in the very large value, viz. 58·1, of the Trouton constant.

Action on Metals

In its action on metals dry ammonium chloride behaves in one sense as a source of hydrogen chloride in that it yields metallic chlorides and hydrogen. That it is the hydrogen chloride formed by dissociation of ammonium chloride on heating which reacts directly with the metal is not a sufficient explanation, since comparative experiments with dry hydrogen chloride and dry ammonium chloride have shown[11] that the former has little significant effect on some metals. Thus a given concentration of hydrogen chloride, when produced by heating dry ammonium chloride to 250–350°C., is about one hundred times as reactive with copper, about forty times with nickel and silver, and at least five times with iron as it is when in the form of free hydrogen chloride alone, and since the hydrogen liberated in the reaction involving ammonium chloride is substantially free from nitrogen any decomposition of ammonia must be ruled out. To explain these phenomena some workers[12] have made use of the theory that many of the 'onium' salts are, in the fused and solid states, acids in the Brönsted sense of the term, i.e. they give rise to cations having a tendency to split off a proton. For example, pyridinium hydrochloride, a typical 'onium' compound, reacts in the fused state with various metals and metallic oxides much as does hydrogen chloride in aqueous solution, and oxides of some of the rare earth metals such as lanthanum, neodymium, samarium and yttrium react with solid ammonium chloride to give the corresponding rare-earth metal chlorides with liberation of ammonia. The action of ammonium chloride, one of the simplest 'onium' salts, in the vapour state on metals would on this theory be explained by the ammonium ion NH_4^+ behaving as a cation acid. Since there is no doubt now that in the vapour state ammonium chloride is completely dissociated, this mechanism would require a momentary recombination of ammonia and hydrogen chloride on the surface of the metal with transient formation of the cation acid NH_4^+.

Though the theory of cation acids may be useful to explain the behaviour of ammonium chloride with metals in the absence of oxygen, it does not seem necessary when oxygen or air is present because in that case the hydrogen chloride produced by dissociation of ammonium chloride is first oxidized to chlorine which is then able to attack the metal to yield the chloride. For example, rhodium, palladium, iridium and platinum when heated with ammonium chloride in the presence of oxygen and an alkali metal chloride, e.g. cæsium chloride, yield double chlorides, for example Cs_2PdCl_4, and this reaction does not take place in the absence of oxygen.[13] Platinum and palladium when heated with ammonium chloride at 250–400° in the presence of air yield chlorides, the reactions being promoted by iron and copper but not by nickel. Platinum and palladium can also react in this temperature range in the presence of iron oxide to give water-soluble compounds among which are complex chlorides containing ammonia or ammonium groups as well as platinum or palladium.[14, 15] Most of the common metals and alloys are corroded by heating in air with ammonium chloride at 200–300°.

Aqueous solutions of ammonium chloride are similar in some respects to dilute solutions of hydrogen chloride in their effect on magnesium, zinc and aluminium. The velocity of the reaction between magnesium and ammonium chloride solutions is much reduced in the presence of added ammonia, and does not appear to be affected by the concentration of hydrogen ions produced by the hydrolysis of the ammonium chloride.[16, 17] Liquid ammonia solutions of ammonium chloride react with metals in a manner resembling that of aqueous hydrochloric acid, though the rate of reaction in liquid ammonia is much slower. Since in liquid ammonia ammonium chloride is partly dissociated into ammonium and chloride ions, the ammonium ion may be considered, as already mentioned, to function as a cation-acid, the equilibrium being expressed by the equations:

$$\begin{array}{ccl} NH_4Cl & \rightleftharpoons & NH_4^{\cdot} + Cl^- \\ & & \;\downharpoonleft\!\upharpoonright \\ & & NH_3 \rightleftharpoons H^{\cdot} \end{array}$$

Sodium, for example, dissolves in a liquid ammonia solution of ammonium chloride to give sodium chloride and hydrogen, whilst beryllium gives beryllium chloride containing ammonia of crystallization, and hydrogen,[18] as well as ammono-basic beryllium chlorides, $BeCl_2,Be(NH_2)_2,xNH_3$, if excess of the metal is present.

Action on Compounds

OXIDIZERS

When heated with powerful oxidizing agents ammonium chloride may yield nitrosyl chloride or chlorine or both. The reaction with nitric acid for example,

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though known for a long time, has been further studied in recent years[19] and has been shown to proceed at 100° according to the scheme:

$$8HNO_3 + 6NH_4Cl \rightarrow 2NOCl + 2Cl_2 + 6N_2 + 3O_2 + 16H_2O$$

no ammonium nitrate being formed. On the other hand, at 85° and 75° ammonium nitrate is formed in approximate yields of respectively 23% and 55–67% according to the equation:

$$NH_4Cl + HNO_3 \leftrightarrows HCl + NH_4NO_3$$

Potassium perchlorate is quantitatively reduced by ammonium chloride in the presence of platinum and this reaction may thus be used for determining the perchlorate. Alkali metal nitrates and arsenates and alkaline earth metal arsenates are readily converted quantitatively into the corresponding chlorides when heated at 350–450°.[20]

Many oxides react completely when heated with dry ammonium chloride to give the corresponding chlorides.[21] Among these are rare-earth oxides, magnesium oxide, cadmium oxide, lead monoxide, lead dioxide, antimony trioxide, manganese dioxide and ferric oxide. Calcium monoxide and barium monoxide react slowly, and cuprous oxide, vanadium pentoxide and nickelous oxide yield products of indefinite composition. Zinc oxide differs from cadmium oxide in first giving a zinc chloride ammine $ZnCl_2,NH_3$ from which ammonia may be split off by further heating. Uranium oxides give uranyl chloride. The carbonates of magnesium, calcium, zinc and manganese behave like the corresponding oxides.

With other chlorine compounds and halides ammonium chloride reacts in a variety of ways. For example with carbon tetrachloride[23] there is no apparent reaction at pressures up to one atmosphere and temperatures up to 400°C., but when heated together in an evacuated tube at 450–475° to a pressure of about 20 atmospheres melon ($C_6H_3N_9$) is formed. In contrast no reaction takes place with chloroform. With bromine trifluoride ammonium chloride reacts explosively,[23] and with arsenic chloride complex compounds are formed.[24] With montmorillonite–silver chloride, ammonium chloride and some other chlorides, including those of sodium and mercury, give complexes having the same chemical properties as montmorillonite–silver chloride; of these complexes that with ammonium chloride is the most stable.[25]

SULPHATES AND GLASS

Alkali metal sulphates when dry are changed smoothly and completely into the corresponding chlorides when heated to 350–450° with ammonium chloride.[20] In contrast alkaline earth sulphates do not appear to react so readily, for example even at 950° only 84% of barium sulphate is converted into chloride.[26]

By heating lithium borohydride with ammonium chloride in the absence of a solvent to approximately 230° borazole, $B_3N_3H_6$, is formed[27] in yields of 30–35%, which though of the same order of magnitude as those obtained by Stock's original method are achieved more conveniently since high pressures, high-vacuum apparatus and diborane as a starting point are not required. At higher temperatures above about 275° borazole reacts with ammonium chloride to give B-monochloroborazole, $B_3N_3H_5Cl$, and hydrogen.

When glass, even hard borosilicate glass, is heated in contact with solid ammonium chloride it is attacked.[28] After two or three hours at about 500° for example the surface is visibly etched. A possible mechanism for this effect is reaction between free sodium ions, which are known to occur in glass, and the strongly polar ammonium chloride and the hydrogen chloride produced by dissociation. Some glazes are attacked when heated with ammonium chloride owing to volatilization of lead compounds.[29]

SOURCE OF CHLORINE, HYDROGEN CHLORIDE AND AMMONIA

Some reactions of ammonium chloride with various salts and oxides form the basis of process patents for manufacturing chlorine, or hydrogen chloride and ammonia. In one of these[30] ammonium chloride is separated from the end-liquors of an ammonia–soda process and heated with manganous oxide to form manganous chloride and ammonia, the latter being returned to the process. The manganous chloride is then treated with manganese dioxide and nitric acid in towers to give chlorine and manganic nitrate. Manganese dioxide and nitric acid are regenerated from manganic nitrate by spraying a concentrated solution of the latter into a fluidized bed of manganese dioxide. Another example[31] is the reaction between ammonium chloride and magnesia at 500–600° to give ammonia and magnesium chloride, the latter being subsequently treated with steam to give hydrochloric acid and regenerate magnesia. In another of these processes[32] ammonium chloride is mixed with molten sodium bisulphate and circulated through two stripping zones, the first at 220–270° for hydrogen chloride, the second at 330–380° for ammonia. In yet another,[33, 34] ammonium sulphate, alone or mixed with sodium sulphate, is heated with ammonium chloride to yield hydrogen chloride and reform ammonium sulphate.

OXIDES AND SULPHIDES

Aqueous solutions of ammonium chloride react with some oxides and hydroxides and carbonates, but not with others.[35] For example, cold saturated solutions do not react with cuprous oxide, alumina, oxides of lead, stannous oxide, ferric oxide or uranyl oxide, but they convert silver oxide into silver chloride, form oxychlorides with cupric hydroxide, mercuric hydroxide, nickelous hydroxide and cobaltous oxide, and form soluble complex chlorides with the hydroxides of magnesium, zinc and cadmium, and with stannic hydroxide, manganous hydroxide and ferrous hydroxide.

The sulphides of copper, silver, mercury, tin, lead, bismuth, cobalt, nickel, tungsten and uranyl do not react with saturated solutions,[36] whilst those of cadmium, antimony, molybdenum, manganese and iron are readily attacked by cold solutions yielding the corresponding metal chlorides. This behaviour towards ammonium chloride may be used to distinguish between the sulphides of molybdenum and tungsten.

MISCELLANEOUS REACTIONS

A saturated solution of ammonium chloride may be used instead of hydrochloric acid in making up aqua regia. The mixture converts silver bromide, iodide and cyanide into silver chloride; slightly attacks lead sulphate but converts lead chromate into the chloride; reacts vigorously with mercuric sulphide and silica; but does not attack barium sulphate, calcined alumina, chromium sesquioxide and titanium dioxide.[37]

Ammonium chloride solutions precipitate silica gels from solutions of sodium silicate, and increase the setting rate of plaster of Paris by increasing the initial rate of formation of gypsum nuclei; a 0·25 N. solution doubles the rate of setting and a 2 N. solution raises it more than five-fold, but some reduction in tensile strength of the set plaster occurs at the same time.[38, 39] Other reactions accelerated by ammonium chloride include that between copper and ammonia in cuprammonia preparation,[40] and the development of colour in heated furfural solutions which is a suspected contributory cause of 'browning' in sugar solutions and various food products.[41] On the other hand the precipitation of calcium tartrate from solutions is retarded by the presence of ammonium chloride.[42]

Liquid ammonia solutions of ammonium chloride react with oxides and hydroxides of some metals to give the corresponding chlorides.[43, 44] As already mentioned (see page 423), the tendency of the cation-acid NH_4^+ to split off a proton is probably responsible for these reactions. In this connection it is interesting to note that two independent methods[45, 46] have shown that the undissociated portion of ammonium chloride dissolved in liquid ammonia is partly associated bimolecularly.

Corrosion of Metals and Alloys

STEEL

In aqueous solution ammonium chloride, like other ammonium salts of strong acids, is hydrolysed and the solution is acid in reaction; for example a molar solution has a pH value of about 5 at 20°C. For this reason solutions of ammonium chloride are markedly corrosive towards many metallic materials of construction. Even solid ammonium chloride is corrosive if surrounded by a humid atmosphere and under these conditions it attacks susceptible metals with which it comes into contact; for example airborne ammonium chloride dust settling on to mild steel or cast iron can cause star-shaped areas of corrosion consisting of central pits with irregular lines of corrosion products radiating outwards. The corrosion rate of steel in contact with solid ammonium chloride decreases as the relative humidity rises beyond 70%.[47] This is in direct contrast with the rate when in contact with ammonium sulphate which increases with increasing relative humidity values up to 100%. A possible explanation is that the primary corrosion product, namely ferrous chloride partially oxidized to ferric chloride, reacts with ammonia from the hydrolysed ammonium chloride to give a hydrated ferroso-ferric oxide in the form of a gel surrounding the particle of ammonium chloride. At the higher relative humidities the gel is continuous and prevents the spread of solution from the particle of hygroscopic ammonium chloride, but at lower humidities it is discontinuous and allows solution to spread and cause further corrosion along filiform tracks. In support of this explanation it has been observed that at relative humidities above about 95% the corrosion spots are localized round the particles of ammonium chloride, whilst as the relative humidity decreases the filiform growth increases until at 70% R.H. most of the surface appears to be attacked. With ammonium sulphate the course of corrosion is the opposite, the filiform corrosion becoming more in evidence as the relative humidity rises to the maximum. Mild steel and cast iron are suitable for use with cold solutions of ammonium chloride up to strengths of about 5% if corrosion rates of the order of 0·5 mm. per year are not objectionable, and in general it is reasonably economic to use steel and cast iron in contact with such solutions if iron contamination can be tolerated.[48] The high-silicon irons containing 14–15% silicon are claimed to show losses in thickness of as little as 0·05 mm. per year in solutions of all concentrations up to the boiling point. Substantial resistance to general corrosive attack is shown by the chromium–nickel stainless steels and by the chromium steels.[49, 50] These are prone, however, to suffer a pitting type of corrosion which can lead to local failure even though the overall loss of metal from the surface is as low as 0·025 mm. of thickness per year. There is some evidence that the previous history of the chromium–nickel stainless steel has an influence on its resistance to attack; for example, the higher tensile materials are not so resistant as those that have been air-cooled from 1200°C. or water-quenched from the same temperature. Pitting may occur even in cold solutions and it becomes severe at the b.p. Stress-corrosion also occurs in chromium–nickel stainless steels exposed to boiling solutions of ammonium chloride and under stresses greater than about 10,000 lb./sq. in.[53] Pitting apart, however, the stainless steels show negligible corrosion as measured by overall loss of thickness in solutions of up to about 20% strength at temperatures up to the boiling point. Nickel–chromium–molybdenum stainless steels show good resistance.[51, 52]

OTHER METALS

Copper, brass and bronze are fairly resistant in the absence of oxygen, but corrode rapidly in the presence of air especially at the air/solution interface. Particles of ammonium chloride do not seriously corrode copper at relative humidities below 80%.[54] The degree of attack on zinc depends on the purity of the metal.[55] Thus pure

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zinc is only slightly attacked in 10% solutions; 0·02% of iron greatly increases the attack, perhaps owing to the low overvoltage of iron for hydrogen; cadmium has an effect similar to that of iron. Lead on the other hand reduces corrosive attack to a minimum when present to the extent of 1%, probably owing to its homogenizing action on zinc. Nickel and its alloys show a fair degree of resistance and lead is resistant to cold solutions of all strengths. Titanium and zirconium have been reported to show negligible corrosion rates in solutions of up to 10% strength up to 100°C. In boiling saturated solutions zirconium was found to be unaffected and titanium showed a shallow blister type of pitting sparsely scattered over the surface, though the overall corrosion rate was negligible.[50]

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USES

In Dry Batteries and Galvanizing

Ammonium chloride is an important industrial chemical of which the two largest uses are, in order of magnitude, in the manufacture of dry batteries and in galvanizing. Dry batteries, which are made on a very large scale, differ in details of construction, but all contain a stiff starch paste embodying the depolarizer, manganese dioxide, graphite or carbon, and ammonium chloride, sometimes with a small proportion of zinc chloride. This paste, in which ammonium chloride (and zinc chloride if present) functions as the electrolyte, surrounds the carbon rod that serves as positive pole and fills the space between it and the cylindrical zinc container that forms the negative pole. Sometimes a layer of a thinner paste of ammonium chloride, or ammonium chloride and zinc chloride, and starch is interposed between the walls of the container and the stiff paste. Besides zinc chloride, other salts are sometimes added to the ammonium chloride for special purposes. Lithium chloride and calcium chloride, for example, enable dry batteries to operate with reasonable efficiency at temperatures below 0°,[1, 2] but they reduce the output at normal temperatures. It is remarkable that all attempts to improve dry-battery output by using salts other than ammonium chloride and zinc chloride have failed. Some of the reasons for this are bound up with the buffer capacity, conductivity and solubility of mixtures of these two salts[3] and their interrelation with manganese dioxide.[4–6]

In galvanizing, sheet steel or other steel articles are degreased and pickled in sulphuric or hydrochloric acid containing an inhibitor to remove oxide scale, washed free from acid and then pushed downwards through a layer of ammonium chloride into molten zinc on which the ammonium chloride floats. Some zinc chloride is often mixed with the ammonium chloride. The purposes of the ammonium chloride are to ensure that the metal surfaces enter the molten zinc free from oxides and to keep the surface of the zinc away from the atmosphere and thus prevent undue wastage by oxidation. Even so, some oxidation does occur and it is often considered worth while to recover zinc compounds from the skimmings of galvanizing baths, either as zinc chloride or as zinc ammonium chloride, both of which may be used again.[7–9] Ammonium chloride is also used as a flux in metal coating, for example the tinning of copper, and in general soldering when mixed with other materials to form pastes.[10–13] A method recently described of making use of its fluxing properties in brazing and soldering metals admits it in the form of vapour (dissociated) to the assembly at joining temperature and then flushes it away with a non-reactive gas when the joint is secure.[14]

In Metallurgy

As well as finding a major outlet in galvanizing, ammonium chloride has several minor metallurgical uses, for example in mixtures for tempering steel[15]; in the preparation of chrome spinel (Cr_2O_3,MgO,Al_2O_3) for use as a refractory[16]; in flotation processes for its protective action in preventing formation of lime films on pyrites surfaces[17–19]; in the recovery of vanadium from bauxite residues,[20] and in the chromizing of iron and steel. It finds uses also in the electrolytic polishing of nickel[22]; in the electrolytic refining of iron[23]; together with other salts in the refining of molten copper, zinc, tin and their alloys[24]; for preventing contraction loss during casting of nodular iron[25]; in reducing loss of molten type metal by surface oxidation,[26] and in chemical colouring of copper alloys.[27] Very finely divided ferric oxide can be made by tumbling iron shavings in a 10% solution of ammonium chloride in closed barrels.[28]

In Building Materials

Ammonium chloride may be used in a variety of ways in certain building materials. For example it increases the rate of hardening of gypsum cements,[29] and of Portland cement when added, dissolved in the gauging water, in the proportion of 0·25–1·0% of the weight of the cement; it may alternatively be added to the cement clinker prior to grinding and so be embodied in the cement.[30, 31] It is more usual, however, in current concrete practice to employ calcium chloride for this purpose, though ammonium chloride may be said to have some advantage over calcium chloride (when introduced into the cement through the clinker) in not being hygroscopic. Mixed in a slurry with iron filings, or with iron filings and a suspending agent such as sodium carboxymethylcellulose, it forms water-proofing compositions for concrete and general masonry.[32, 33] Together with linseed-oil, rosin and bleaching powder it forms a foaming agent for Portland cement or gypsum plasters,[34] and when heated with magnesium oxide at 220–400° solid ammonium chloride yields a magnesium oxychloride cement requiring only addition of water for setting.[35] The presence in the mixing water of ammonium chloride overcomes the undesirable excessive expansion that mortars and plasters are subject to when made with magnesia and dolomitic limes,[36] whilst addition of about 1% of the salt to colloidal starch gels containing inert inorganic materials such as talc, alumina and graphite confers sufficient thixotropy on the mixtures to allow them to be 'thrown' on potters' wheels.[37] The reactivity of various calcareous cementitious materials may be measured by the rate of evolution of ammonia when the sample is boiled with excess of ammonium chloride solution.[38]

As Fertilizer and Fire-retardant

Ammonium chloride has been proposed as a fertilizer on several occasions, but it probably can compete with established materials only when it is in surplus. Further the effect on some plants of a high concentration of chloride ions in the soil may be unfavourable. On the other hand, for plants that are unaffected by chlorides, ammonium chloride is as good a source of nitrogen as any of the commoner nitrogenous fertilizers. When combined with certain other fertilizer materials ammonium chloride may be more generally suitable. For example a mixed calcium phosphate–ammonium chloride fertilizer may be made by causing mono-calcium chlorophosphate to react with ammonia,[39] and it has been suggested to make a similar mixture by treating the ammonium chloride liquors produced in the ammonia–soda process with phosphoric acid and calcium chloride.[40] A mixed calcium carbonate–ammonium chloride fertilizer may also be derived from the end-liquors of an ammonia–soda process.[41] Ammonium chloride is also used in agriculture in a minor way as a constituent of anticryptogams,[42] fungicides[43] and together with sodium nitrite as a gas-generating mixture for dispersing vaporizable pesticides.[44]

Ammonium chloride behaves as a fire-retardant and for this purpose is usually applied to materials in the form of a solution.[45, 46] Some fabrics, particularly cotton, are made tender by the treatment.[47] Fire hazards in large piles of coal may be reduced by ammonium chloride,[48] and it also functions as a flame attenuator

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when mixed with or surrounding explosives used in mines subject to explosion risks due to firedamp or to dusts, for example in sulphur mines.[49, 50] On the other hand ammonium chloride mixed with sodium nitrite forms the basis of the well-known flame-free explosives ('Hydrox') that are safe for use in gassy mines. The source of the explosive force is the generation of nitrogen by the interaction of the two salts.[51]

Miscellaneous Uses

Ammonium chloride has a large number of small uses depending for their realization on the various ways in which it can behave, for example as an electrolyte, as a source of hydrogen chloride and ammonia, and as an acid. Among these may be mentioned its use in the manufacture of anhydrous magnesium chloride by heating with magnesia[52]; in making adhesive lignin resins[53]; as a complex with calcium sulphonate for use as a lubricating oil additive[54]; to replace sodium chloride for preserving meat for people on sodium-free diets[55]; as a component of acid fixing baths in photography[56]; mixed with copper for deoxygenating air in enclosed electrical gear.[57] Other minor uses are in hair-waving preparations[58–60]; as a stabilizer of rubber latex and colloidal solutions, for example of rosin[61–63]; to improve brightness in calcium phosphate phosphors[64]; for accelerating the melting of glass,[65, 66] for improving the chemical resistance of glass surfaces by de-alkalizing them,[67] for extracting nickel and magnesium compounds and silica from serpentine,[68] for modifying the surface structure of silica gels prepared by the action of formaldehyde on sodium silicate,[69] and for repelling package-penetrating insects.[70] Electrolysis of ammonium chloride solutions containing alkali metal or alkaline-earth metal chlorides has been suggested as a way of obtaining substantially pure chlorine and recovering ammonia.[71] A mixture of 80% of silicon carbide and 20% of ammonium chloride can be used for silicon cementation or carburizing low-carbon steels and high-carbon chromium steels by heating in contact with them at 800–1100°C. The mechanism of the process is not fully understood, but it has been suggested that decomposition of the ammonium chloride liberates silicon tetrachloride which is adsorbed on the surface of the steel and causes diffusion of silicon.[72] Carbon for electrodes for air-depolarized wet cells may be activated by means of ammonium chloride.[73]

As Catalyst

Ammonium chloride behaves as a catalyst mainly in certain organic reactions, for example in the reduction of nitro compounds by iron and hydrochloric acid to give the corresponding amines[74]; in the ammonolysis of esters in liquid ammonia to give amides,[75] and of oils and fats to give long-chain fatty acid amides[76]; in the dissociation of glycols and aliphatic mono-olefines to give *cyclo*-olefine hydrocarbons,[77] in the conversion of alkyl ketones to polyalkylbenzenes[78]; together with cuprous chloride in various polymerizations involving chloroprene[79] and in the manufacture of vinylacetylene[80–82] and of vinyl chloride.[83] In most of these reactions the catalytic activity of the ammonium chloride springs from its ability to introduce hydrochloric acid into the environment, either through hydrolysis in solution or dissociation in the gaseous phase. In some other reactions, for example in the preparation of acetal from acetaldehyde and ethyl alcohol,[84] the ammonium chloride is thought to function as a true catalyst. Another type of catalytic activity exhibited by the salt may be exemplified by its effect on the initial reaction between phenol and formaldehyde in resin formation, in which it first reacts with formaldehyde to give hexamethylenetetramine and hydrochloric acid, both of which then catalyse the condensation reaction.[85] Other examples of the behaviour of ammonium chloride as a catalyst or promoter or as a component of reaction-promoting mixtures may be found in coal hydrogenation[86–89]; in butanol–acetone fermentation processes[90, 91]; in the isomerization of paraffins[92]; in the polymerization of acetylene[93]; in the preparation of acrylonitrile from hydrogen cyanide and acetylene[94] and of sorbitol from starch, dextrin and other carbohydrates.[95] The thermal decomposition of potassium perchlorate is much influenced by ammonium halides, the reduction to chlorate and chloride being apparently due to a catalytic effect of the halide anion which increases with the atomic weight of the halogen.[96]

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SECTION X

AMMONIUM BROMIDE

BY J. D. RICHARDS

PREPARATION

Ammonium bromide can be manufactured from bromine and ammonia, or from iron bromide, Fe_3Br_8, and ammonia, or from bromine and ammonium carbonate[1] according to the equation[1]:

$$3(NH_4)_2CO_3 + 3Br_2 = 5NH_4Br + NH_4BrO_3 + 3CO_2$$

the bromide being separated by fractional crystallization. In the processes using elementary bromine, any excess of this element remaining in solution is removed by adsorption on charcoal. Other authors[2–4] describe the manufacture of Fe_3Br_8 from iron scrap, steam and bromine vapour; the bromine is obtained from the mother liquors of the potash industry,[3] and the ammonium bromide is then made by treating a solution of the iron bromide with ammonia, thus precipitating iron oxide, Fe_3O_4.[1, 3] Ammonium bromide may also be produced by the direct action of ammonia on bromine under water,[1, 2] according to the equation:

$$8NH_3 + 3Br_2 = 6NH_4Br + N_2$$

Care must be taken to keep the solution alkaline and so prevent the formation of explosive nitrogen tribromide, NBr_3. Traces of ammonium bromide are reported to occur in commercial bromine,[5] and samples of ammonium bromide contained traces of zinc.[6]

Large crystals of ammonium bromide can be prepared from a saturated aqueous solution by the addition of wood extracts or other vegetable extractives such as pectin or hydropectin.[7]

PHYSICAL PROPERTIES OF AMMONIUM BROMIDE

The density of ammonium bromide, measured by a flotation method,[8] is 2·429, and refractivity[8, 9] (n_D^{25}) has been determined as 1·71239. Dispersions for other wavelengths[9] n_C and n_F are 1·705 and 1·729 respectively, whilst the Abbé number $\{\nu = (n_D - 1)/(n_F - n_C)\}$ is 29·7. The melting point is 541·9°.[10] The heat of hydration of ammonium bromide[11] obtained from measurements of heats of saturation and values of lattice energy is 150 kcal. at 25°, and the latent heat of sublimation[12] at the same temperature is 44·9 kcal./mole. Calculation of the lattice energy of the cæsium chloride type lattice by the Born–Mayer method yields a value of 154·0 kcal./mole.[13]

The thermal expansion (α) of the ammonium bromide crystal, measured by interferometric methods[14] up to 125°, is given by the equation:

$$\alpha_t = 0{\cdot}000{,}055{,}53 + 0{\cdot}000{,}000{,}1216t + 0{\cdot}000{,}000{,}001{,}852t^2$$

The elastic constants[15] for a single crystal of ammonium bromide have been measured by ultrasonic piezoplate methods. The results are quoted in Table I, where C_{11}, C_{12} and C_{44} are the elastic constants for three directions of measurement.

Table I.—Elastic Constants for Crystalline Ammonium Bromide

C_{11}	C_{12}	C_{44}	Bulk modulus	
			Calculated	Observed
2·96	0·59	0·53	1·38	1·63

The dielectric constant has been determined by the plate-displacement method[16] as 7·08.

Structure and Transitions

Huggins[17] determined the diameter of the hydrogen atom in the centred cubic form of ammonium bromide as 1·64 A. Nuclear magnetic investigations by different authors[18–21] have given, for the N–H bond distance in the ammonium radical, 1·025 ± 0·005 A.,[18] 1·03 ± 0·01 A.[19] and 1·035 ± 0·01 A.[21] Proton magnetic resonance widths and relaxation time studies give the line width transition temperature in ammonium bromide as −174°,[19] but other authors report −165°[20] and −171°.[21] The proton line width of the salt is of the order of 20 gauss at −183° to −178°; within a temperature interval of 7° to 20° the line width changes to between 3·5 and 5·3 gauss and this value remains unchanged up to room temperature.[20] Nuclear magnetic resonance study[22] of the bromine nuclei in ammonium bromide shows that in phase I (above 138°) the chemical shift is $1{\cdot}3 \times 10^{-4}$ A. and the spin lattice relaxation time (T_1) is 33 millisecs. for ^{81}Br at 155°. In phase II (−38° to 138°) bromine resonance shows a paramagnetic shift of $2{\cdot}3 \times 10^{-4}$ sec., and T_1 is $0{\cdot}59 \times 10^{-4}$ and $2{\cdot}5 \times 10^{-4}$ sec. at 12° and 104° respectively for ^{81}Br. Some covalent bonding or type of hydrogen bonding exists between neighbouring ammonium and bromide ions, so that when the ammonium ion has such an orientation, one of its four hydrogen atoms takes the position nearest to the bromide ion. In phase III (below −38°) bromine resonance disappears if a crystal powder is used, but in a single crystal a line is observed corresponding to the transition $m = \frac{1}{2} \leftrightarrow -\frac{1}{2}$. The magnetic susceptibility[23] of ammonium bromide is $0{\cdot}429 \times -1 \times 10^{-6}$ c.g.s. units, and although measurements made at the temperature of the lattice transition show very small variations, these are probably due to a change in atomic arrangement and not in electronic state.[24] A general discussion on susceptibility and submolecular structure[25] includes the salt with many others.

The length of the unit cube of body-centred NH_4Br is reported as 4·047 A.[54] or 3·99 A.[50] Irradiation by *X*-rays below −50° causes photochemical decomposition which increases with decreasing temperature.[55, 56] An absorption band is observed at 3·25 e.v., the position and width of which are independent of temperature[56]: it is thought, therefore, that the band is due to the neutral ammonium radical and not to colour centres.

Heat Conductivity and Compressibility

Heat conductivity measurements under pressure from 0 to 1425 kg. cm.$^{-2}$ and at temperatures to within 0·01° of the discontinuity point, show a finite discontinuity at −28° at 1430 atmospheres, and thus indicate a phase change. The temperature of the heat capacity discontinuity is a linear function of the pressure applied. The dielectric constant[27] of powdered ammonium bromide measured from 0° to −50° at 700 kc. sec.$^{-1}$ shows a fall in value at −30·5° and at −38°, the transition temperatures. The temperature coefficient is approximately 0·0009. The compression of ammonium bromide under pressure of 50,000 kg. cm.$^{-2}$ at room temperature and the temperature of solid carbon dioxide has been determined by Bridgman[28] as 0·1676 and 0·1557, respectively. The same author records the compressions for decrements of 0 to 50,000 kg. cm.$^{-2}$ and of 50,000 to 100,000 kg. cm.$^{-2}$ as 0·170 and 0·074 respectively, illustrating the fact that the substance is initially more compressible.[29] The volume–pressure isotherm[30] at −72° shows a discontinuity at 1620 kg. cm.$^{-2}$ which may indicate a polymorphic transition. The accompanying thermal effect is about 160 g.-cal./mole, and the volume effect approximately −0·017.

Structure of Deutero-ammonium Bromide

Neutron diffraction studies[31] of the crystal structure of deutero-ammonium bromide in four phases show that the low temperature cubic form contains ordered parallel ND_4^+ ions, and in the tetragonal crystal adjacent strips of ammonium ions are antiparallel with bromide ions displaced towards a square array of nearby deuterium atoms. At room temperature the bromide contains deuterammonium ions at random in two orientations, but the high temperature cubic form contains ions in which 1, 2 or 3 deuterium atoms make minimal approach to bromide neighbours. The length of the N–D bond is 1·03 ± 0·02 A., which agrees with the length of the N–H bond in normal ammonium bromide.[18, 19, 21] *X*-Ray diffraction patterns are reported by many authors,[32, 33] and the mass absorption coefficient using *X*-rays has been determined by the Küstner method.[34] *X*-Ray study[35] of ammonium bromide at −100° by Ketelaar shows a number of faint lines due to the tetragonal form with protons arranged tetrahedrally around nitrogen atoms. The same author and others[36] report the transformation of solid ammonium bromide from the tetrahedral to the regular form at −39 °; during this transformation the phenomenon of hysteresis was observed over a region of about 0·15°.[36, 37] Photographic recording shows the transition to occur at −38·2°.[38] Below −39° [39] the cubic crystals contract by about 3% along two axes and change by about 2·5% through movement of the bromine along the third axis. In the tetragonal form below −40° the axes *a* and *c* at −71·3° are 5·713 and 4·055 A., or at −145°, 5·697 and 4·046 A. respectively. The *c*-parameter of bromine is 0·02.[40] Data comparing crystal forms, lattice constants and molecular volumes at −30° and −73° for ND_4Br and NH_4Br are given in Table II.

Table II.—Crystallographic Data for Ammonium Bromide and Deutero-ammonium Bromide

	Temperature	Crystal form	Lattice constant	Mol. volume
NH_4Br	−30°	Cubic	4·041 A.	40·00 cm.^{3}
NH_4Br	−73°	Tetragonal	4·034 A.	39·78 cm.^{3}
ND_4Br	−30°	Cubic	4·034 A.	39·78 cm.^{3}
ND_4Br	−73°	Tetragonal	4·034 A.	39·74 cm.^{3}
ND_4Br	−140°	Cubic	3·981 A.	38·33 cm.^{3}

Another transition in ammonium bromide at low temperatures corresponding to that at −104° in the deuteriated crystal is said to occur at −195° on cooling and at −164·5° on warming.[42] Theories[43, 44] of the phase transformations in ammonium bromide and other ammonium halides are confirmed by the data concerning the deuteriated halides obtained by neutron diffraction.[31]

Allotropic or isomorphic crystal transformations are due[45] probably to slip along a plane, and in ammonium bromide crystals (CsCl type) observations of slip[46] show it to be the effect of partial dislocations in the simple cubic lattice along the [100] plane. The tendency for dendritic crystallization of an aqueous solution[47] is increased by gelatin or agar-agar, but suppressed by ferric, cobalt and nickelous chlorides. Drop diagrams of unique crystal patterns can be prepared with the addition of albumin.[48] As with other heteropolar crystals, crystallization originates at the corners.[49] A solution of ammonium bromide in ethyl alcohol gives oriented crystals on [100] and [110] faces of sodium chloride as the crystal planes concerned coincide by all their knots, which is not the case on [111] and [210] faces of sodium chloride on which no orientation is observed.[50] The mutual orientation of ammonium bromide occurs with silver crystals,[51] but many examples of epitaxial growth (i.e. those in which orientation of the newly formed crystal is related to that of the substrate) are not explained in terms of crystal parameters, for example in the crystallization of ammonium bromide on halite,[52] and the absorption of ammonium bromide by precipitated lead sulphide.[53]

PROPERTIES OF THE AQUEOUS SOLUTION

Solubility, Vapour Pressure and Activity

The solubility of[57] ammonium bromide in water at various temperatures is given in Table III. The vapour pressure (p)[58] of moist ammonium bromide measured between 332°K. and 395°K. shows that log p is a linear function of $1/\mathrm{K}^\circ$. The molecular heat of evaporation is 44 kcal. Vapour density measurements indicate complete dissociation between 300° and 400°.

The depression in the vapour pressure of solutions of various concentrations[59] at 100° is given in Table IV. The activity[60] of ammonium bromide has been determined for a solution containing 95 g. in 100 g. of water by measuring the vapour pressure by a dew-point method; the results, given in Table V, show deviations from ideality which are due to association of solvent molecules and dissociation of solute molecules. No abrupt change in the vapour pressure curve occurs on approaching the region of supersaturation.[61]

Table III.—Solubility of Ammonium Bromide in Water

Mole-% of NH_4Br	t°	Mole-% of NH_4Br	t°
60·6	116	81·0	302
63·8	137	82·1	312
64·5	138	83·4	335
65·6	149	85·1	360
66·9	160	85·3	365
70·0	180	86·8	391
70·1	184	97·4	400
72·1	203	88·5	426
73·2	214	90·4	462
75·6	239		
77·7	259		
79·1	285		

Table IV.—Vapour Pressure Depression for Aqueous Solutions of Ammonium Bromide at 100°C.

Weight normal concentration	Depression in v.p. in mm. at 100°
10	228·5
8	190·2
6	145·5
5	121·5
4	99·4
3	74·1
2	48·8
1	23·9
0·5	11·9

Table V.—Activity of Ammonium Bromide in Aqueous Solutions

Observed temperature	Vapour pressure in mm. of pure solvent	Mean dew point	Standard deviation	Partial pressure in mm. of solvent	Activity
35	42·18	29·5	±0·0500	30·92	0·733
40	55·32	33·9	±0·04715	39·67	0·717
45	71·88	38·8	±0·02643	57·60	0·718
50	92·51	43·7	±0·03162	67·20	0·720

Ebullioscopic data[62] for ammonium bromide have given values for the hydration number and a particularly defined equilibrium constant of 4·5 and 2·03 respectively. Later calculations of the dissociation constant at 100° give the results in Table VI,

Table VI.—Dissociation Constants for Ammonium Bromide in Aqueous Solution

n_w	Dissociation constant
2	1·10
3	1·15
4	1·14
5	1·01

where n_w is the weight normal concentration. The same author calculates the hydration of the ions at 100° for NH_4^+ and Br^- as 8 and 3, respectively. The equilibrium constants of the halides, other than the fluorides, of ammonium, sodium and potassium are nearly identical, which suggests that they must be equally ionized.[62] The viscosity of aqueous solutions[63] of ammonium bromide is given by the Jones and Dole equation:

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc$$

where A and B are constants obtained experimentally and c is the concentration in g. moles litre^{-1}. The apparent molal volume[63] is given by the equation

$$\phi = 44{\cdot}25 + 0{\cdot}84\sqrt{c} - 0{\cdot}025c$$

The heat of solution as a function of dilution[64] is characterized by a marked absorption of heat up to the formation of a saturated solution and a smaller absorption during gradual dilution.

Optical Properties

Investigation of the magneto-optic anomaly of certain cubic crystals[65] using a crystal of ammonium bromide of thickness 0·746 cm. and specific gravity 2·325 in a field of 9780 œrsteds gave the results set out in Table VII.

Table VII.—Magneto-optic Anomaly of Ammonium Bromide

Wave-length, A.	Magnetic rotation $2p$	Verdet constant	Magneto-optic anomaly γ %
5893	12·28°	0·0504	69·0
5461	14·61°	0·0601	69·8
4358	25·29°	0·1040	69·5

Investigations[65] of the magneto-optic anomaly of a solution of specific gravity 1·297 containing 75·08 g. ammonium bromide/100 g. of water in a column thickness of 1·767 cm. and magnetic field 8450 œrsteds gave the results in Table VIII. Optical dispersions[65] (η) of the same solution are given in Table IX.

Table VIII.—Magneto-optic Anomaly of Ammonium Bromide Solutions, d 1·297

Wave-length, A.	Magnetic rotation	Verdet constant	Magneto-optic anomaly γ %
5461	13·68°	0·0275	83·2

Table IX.—Optical Dispersions of Ammonium Bromide Solution, d 1·297

Wave-length, A.	η
5893	1·40915
5461	1·41146
4358	1·42127

Electrolysis

The conductivity coefficient for aqueous ammonium bromide is said to be[66] independent of the nature of the electrolyte, but dependent on the total concentration of all ions in the solution. This is confirmed by experiments on many other uni-univalent electrolytes. Electrolysis of an aqueous solution of ammonium bromide[67] follows the equations:

$$\text{(i)}\ 2NH_4^+ + 2^= \rightarrow 2NH_3 + H_2 \qquad \text{(ii)}\ 2Br^- + 2^+ \rightarrow 2Br \rightarrow Br_2$$

The bromine reacts with ammonium bromide forming hydrogen bromide and bromamine, NH_2Br, which splits up into ammonium bromide, nitrogen and bromine. At higher temperatures the bromine forms ammonium hypobromite, NH_4BrO, which then reacts with more hydrogen bromide as follows:

$$NH_4BrO + 2HBr = NH_4Br + H_2O + Br_2$$

Thus bromine, hydrogen bromide, nitrogen and a little oxygen are liberated at the anode, and it is owing to the decomposition and the reactions of bromamine that bromine cannot be efficiently produced by electrolysis of ammonium bromide.

Freezing point determinations of dilute solutions show a factor operative with ammonium bromide which is similar to association,[68] but is negligible with other uni-univalent salts. Accompanying the orderly freezing of dilute aqueous solutions is an electrical effect[69] which may be as great as 84 v. across the water–ice interface. This may have a bearing on the electrical effects associated with thunderstorms. Light scattering[70] measurements on aqueous ammonium bromide solution show little deviation from values calculated from the Einstein–Debye theory and the Verdet constants; optical dispersions[71] and molecular rotations[72, 73] have been measured and from these other data can be calculated for the composite ions.

PROPERTIES OF NON-AQUEOUS SOLUTIONS

Liquid Ammonia Solutions

Normally the apparent molar volume of a dissolved salt increases with increase in concentration. This occurs in aqueous solutions of ammonium bromide, but to a much larger extent in liquid ammonia solutions, although the values of the apparent molar volume in ammonia are considerably smaller than those in water for the same mol.-fraction concentration.[74] The solubility of the salt in liquid ammonia at $-33{\cdot}9°$ is 90·75 g./100 g. of NH_3,[75] and 51 g./100 c.c. of solution[76] at $-35°$. The solubility of the bromide exceeds that of the chloride; both of these lie between the data for the iodide, which is very soluble, and the fluoride which is very much less soluble.[77] The osmotic coefficient[78] lies between those of ammonium chloride and iodide; it is greatest for the iodide. The density of solutions of ammonium bromide in liquid ammonia at 15° is 0·641 and 0·817 for concentrations of 3·89 g./100 g. NH_3 and 38·56 g./100 g. NH_3, respectively. The vapour pressure lowerings[78] for varying concentrations of ammonium bromide in liquid ammonia are given in Table X.

Table X.—Vapour Pressures of Solutions of Ammonium Bromide in Liquid Ammonia

Concentration, moles/1000 g. of NH_3	0·198	0·708	2·956	4·317
Vapour pressure lowering at 15°, mm.	17	58	240	381

The decomposition potential of ammonium bromide in liquid ammonia[79] is 0·92 v., as compared with 1·46 v. for the aqueous solution. The nitrogen overvoltage (η)[80] on platinum in the electrolysis of the ammonia solution between current densities of $i=10^{-6}$ and $i=10^{-3}$ amp./sq. cm. is over 1 v., and is given by $\eta=\text{constant}+0{\cdot}085\pm0{\cdot}05i$ for a 0·2 N. solution.

Heats of solution of ammonium bromide in liquid ammonia and of reaction with various compounds in this solvent have been determined.[81–83] Ammonium bromide reacts with sodamide and potassamide in liquid ammonia according to the equations:

$$\text{(i)}\quad NH_4Br+NaNH_2 \rightarrow NaBr,\text{am.}+2NH_3\ (l)$$

$$\text{(ii)}\quad NH_4Br+KNH_2,\text{am.} \rightarrow KBr,\text{am.}+2NH_3\ (l)$$

Data for these reactions at $-33{\cdot}4°$ give the heat of neutralization of the base KNH_2 with NH_4Br[81, 82] as 26·5 kcal. Heats of reaction of lithium, sodium, potassium and cæsium with dilute solutions of ammonium bromide in liquid ammonia at $-33°$, and the heats of solution of the metals in pure liquid ammonia have been used to calculate the heat of reaction of each dilute metal solution with the ammonium ion. These exothermic heats of reaction vary from 39·7 to 41·6 kcal. with a mean value of 40·4 kcal.[84]

Miscellaneous Solvents

Ammonium bromide is soluble in molten iodine bromide which acts as an ionizing solvent, the solution being highly conducting.[85] The solubility in liquid sulphur dioxide[86] at 25° ± 0·002 is 0·052 g./100 g. of solution. The salt dissolves also in concentrated aqueous antimony trichloride solution to give an electrically conducting solution.[87] Ammonium bromide is practically insoluble[88] in titanium tetrabromide ($TiBr_4$, m.p. 39°) and the solution is non-conducting. The solubility in absolute acetone[89] decreases with increase in temperature and the salt is less soluble than the halides of sodium and lithium, the solubilities of which increase with temperature. The viscosity of[90] the methyl alcohol solution decreases with increase in temperature. The solubility in some alcohols[91] is given in Table XI. There is a definite break between values of the solubility at 30° and 40° owing to the change in degree of solvating power of the solvents.

Table XI.—Solubilities of Ammonium Bromide in Certain Alcohols

Solvent alcohol	Solubility of NH_4Br, g./100 g. of solvent									
	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
Methyl	10·62	11·53	12·33	13·09	14·07	14·88	15·63			
Ethyl	2·968	3·154	3·356	3·583	4·260	4·412	4·552	4·709		
n-Propyl	0·9082	1·033	1·158	1·269	1·357	1·397	1·476	1·501	1·576	1·613

The rate of exchange of deuterium[92] between 0·3–0·5 M. ammonium bromide and 0·1–1·2 M. methyl alcohol in dimethylformamide, $H.CONMe_2$, containing 0·0013 to 0·13 M. HBr at 0° is given by

$$\frac{k[\text{salt}][\text{MeOH}]}{[\text{acid}]}$$

The equilibrium constant is 1, since identical rates are found with the deuterium either in the salt or in the methyl alcohol. A negative salt effect occurs and the rate usually decreases with increasing polarity of the solvent; it is found that the rate of tritium exchange is 0·8 times the rate for deuterium. Ammonium bromide solutions in dimethylformamide are electrically conducting[93]; the specific conductance of solutions at various concentrations and at different temperatures is given in Table XII.

Ammonium bromide forms with mercuric chloride a complex salt, $HgCl_2,4NH_4Br$, which is stable even in 0·0005 M. solution.[94, 95]

Table XII.—Specific Conductances ($\times 10^3$) *of* NH_4Br *in Dimethylformamide*

Temperature, °C.		−50	−40	−20	0	20
Concentration, moles solute/1000 g. solvent	0·20	1·21	1·67	2·44	3·40	4·3
	0·50	1·69	2·15	3·63	5·07	6·59
	0·64	1·82	2·34	4·12	5·52	7·15
	0·76	1·83	2·47	4·25	5·99	7·98
	0·90	1·77	2·47	4·35	6·45	8·68
	1·10	1·58	2·32	4·43	6·86	9·25
	1·33	1·54	2·28	4·53	7·14	9·68
	1·66	1·27	2·17	4·48	7·47	—

SYSTEMS CONTAINING NH_4Br

NH_4Br–NH_4Cl and NH_4Br–NH_4I

Thermal analysis[96, 97] and dilatometric measurements[98] of mixed crystals of ammonium bromide and ammonium chloride show transitions near 0° and −36° for 40 mole-% and 8·5 mole-% of the bromide respectively.[96] Previous work[97] had indicated temperatures of +15° and −30°. Dilatometric[98] experiments indicate transitions which rise from −38·4° for pure ammonium bromide to a maximum at 23° for an approximately 50 mole-% concentration of the salt; the transition temperature then decreases until with less than 8 mole-% it becomes imperceptible. In the similar chloride transition, no change is observed with more than 12 mole-% of NH_4Br.[98] Earlier work on specific heats[99] of the mixed crystals showed change-points at temperatures higher than those of the components.

In the system NH_4I–NH_4Br[109] a minimum in the lattice dimension occurs, whereas normally mixed-crystal lattices are additive.

NH_4Br–KBr

In the system NH_4Br–KBr[100–103] true mixed crystals of the sodium chloride type form at concentrations up to 40 mole-% of NH_4Br,[100] and this is confirmed by other studies[101] which show that at + 18° and − 150° at least 36% of the potassium atoms are replaced by ammonium groups.

NH_4Br–$HgBr_2$

Belyaev and Mironov have studied[104–106] the system NH_4Br–$HgBr_2$ up to 75 mole-% of NH_4Br (excess over 75% causes frothing of the melt). The liquidus curve shows a eutectic at 140° corresponding to 48 mole-% of NH_4Br,[104] and the four incongruent melting compounds are set out in Table XIII.[105, 106] Conductivities in the system have been reported by Jander and Brodersen.[107]

Table XIII.—Compounds in the System NH_4Br–$HgBr_2$

$HgBr_2$: NH_4Br mol. ratio	9:2	3:2	1:1	1:2
Mole-% of NH_4Br	24	40·5	60·5	67
Transition temperature on liquidus	222°	165°	201°	266°

NH_4Br–$AlBr_3$

In the system NH_4Br–$AlBr_3$[108] the viscosity–concentration curves are sigmoid and show a maximum corresponding to the compound NH_4Br,Al_2Br_6. At 150° the viscosity of aluminium bromide is 1·4531 and that of 33·33 mole-% NH_4Br is 8·3383 centipoises; at 120° the corresponding values are 1·9462 and 14·4835. The curves of the specific electrical conductance against concentration for the NH_4Br–$AlBr_3$ system are slightly concave towards the concentration axis with no maximum. The specific gravity–concentration curve of the system is concave towards the concentration axis with a maximum at 29·1 mole-% of NH_4Br. The specific gravity at 150° of the 33·33 mole-% solution, corresponding to the compound NH_4Br,Al_2Br_6, is 2·647.

NH_4Br–AgBr–H_2O

The equilibrium constants[110] of solution of silver bromide in aqueous ammonium bromide at 25°, defined as $a_{(NH_4)_2AgBr_3}/a^2_{NH_4Br}$ where a is the activity, are 3·76, 3·33, 3·48, 5·61 and $13{\cdot}2 \times 10^{-4}$ in 1·98, 3·84, 7·94, 14·2 and $27{\cdot}73 \times 10^{-1}$ molar solutions of ammonium bromide, respectively. The activity coefficient of $(NH_4)_2$-$AgBr_3$, which is the resulting compound giving the bivalent ion $AgBr_3^{=}$, is 0·326 in 1 M. solution. The heat of solution of liquid bromine in a suspension of silver in concentrated ammonium bromide solution is 23·81 kcal. mole^{-1},[111] but the heat of solution of silver bromide in the same solvent is nil.

NH_4Br–$PbBr_2$–H_2O

Study of the $PbBr_2$–aqueous NH_4Br system[112] shows that up to 0·6 M. solution of NH_4Br the solubility of lead bromide is not much affected and the solid phase is $PbBr_2$. Between 0·6 and 3·5 to 4·0 M. solution (depending on temperature), the solid phase is $2PbBr_2,NH_4Br$,[112, 113] and the solubility of lead bromide increases rapidly with increasing concentrations of ammonium bromide. Above this concentration (3·5 to 4·0 M.) the concentration of ammonium bromide has little influence on the lead bromide concentration, and the solid phase is $PbBr_2,2NH_4Br$.[112, 113] Lead bromide has little effect on the solubility of ammonium bromide.

NH_4Br–KBr–H_2O and NH_4Br–NH_4Cl–H_2O

The solid phase in the system NH_4Br–KBr solution at 25°[114] shows a transition from the sodium chloride to the cæsium chloride structure at 98·5 mole-% of NH_4Br. A solubility gap occurs between 50·4 and 98·3 mole-% of NH_4Br and therefore the system consists really of two branches. The solid phase of the NH_4Cl–NH_4Br solution system[114] has the CsCl structure, and the system shows a continuous curve which exhibits a minimum. The quaternary system $K^+ + NH_4^+ + Cl^- + Br^- + H_2O$ at[114] 25° shows two solid phases of NaCl and CsCl structures, and the solubility diagrams consist of two fields separated by a 2-salt boundary. The end of the 2-salt line is at 74·2 mole-% NH_4^+ in the Cl^- boundary system and at 75·7 mole-% NH_4^+ in the Br^- system.

Miscellaneous Systems

Gradual addition of ammonium bromide to the eutectic system H_2O–NH_4Cl–NH_4I[115] at 25° displaces the more soluble ammonium iodide to a greater extent than ammonium chloride, resulting in the solution of ammonium bromide at the expense of the water originally bound by the chloride and iodide.

The formation of an $NH_4[SrBr_3]$ complex in aqueous solution containing ammonium and strontium bromides has been established[118] and the salt $CoBr_2,2NH_4Br,2H_2O$ occurs in the system $CoBr_2$–NH_4Br–H_2O.[119] By evaporation in a vacuum of an equimolecular solution of ferrous bromide, $FeBr_2$, and ammonium bromide over sulphuric acid, ammonium bromide crystallizes in fern-like forms, and on further evaporation of the mother liquor pale green crystals of $NH_4[Fe^{II}Br_3],6H_2O$ are obtained.[120] The limits of formation of this salt are 55·1–47·8 g. of $FeBr_2$ and 2·4–9·0 g. of NH_4Br per 100 g. of solution. The salt is very hygroscopic and its *X*-ray pattern is distinct from that of either $FeBr_2$ or NH_4Br.

Cryoscopic examination of the system aluminium chloride–nitrobenzene–ammonium bromide shows that addition of ammonium bromide to the $AlCl_3$–$C_6H_5NO_2$ system causes lowering of the freezing point almost proportional to the amount added. This lowering is assumed to be due to the dissociation of complex compounds which form. Ammonium bromide is insoluble in pure nitrobenzene,[121] but the solubility is increased by aluminium bromide as well as by the chloride.[122] The solution of ammonium bromide in nitrobenzene and aluminium bromide has a higher specific conductance than that of aluminium bromide in nitrobenzene alone, and on electrolysis of the ternary solution bromine is liberated at the anode, but no cathode products are observed probably because any ammonia formed reacts with the electrolyte.[122] Conducting complexes are known to be present in the system aluminium bromide–xylene–ammonium bromide.[126] Various ternary systems of polyvinyl alcohol[123, 124] and water, among them the ammonium bromide system, have been studied in order to determine the hydration of the alcohol, from determination of the ionic strength of solution.

Dendrites[116] produced in the crystallization of ammonium bromide from slightly supersaturated solutions are not monocrystals but consist of single aggregates and grains that have combined rapidly during the crystallization process.[116] Impurities of various cations in the solution have an effect on crystal shape which is characteristic for each cation.[116, 117]

Ammonium bromide lowers the solubility of papaverine hydrochloride in water and small amounts (5%) of ammonium bromide added to a solution render it turbid.[125] Addition of ammonium bromide or other salt (KCl, NaCl, NH_4Cl) to solutions containing ammonia, ammonium nitrate, tartaric acid and a copper salt causes extinction of the colour of the cupric ammonium complex,[127] and ammonium bromide is also found to retard the precipitation of calcium tartrate by interaction of soluble calcium salts with tartaric acid.[128]

CHEMICAL PROPERTIES OF AMMONIUM BROMIDE

Ammonium bromide reacts at high temperatures with alkaline earth sulphates[129]: with strontium sulphate 94% is converted into the bromide. When added to a solution of tetrasodium phosphide, Na_4P_2, and sodium in liquid ammonia,[130] ammonium bromide reacts according to the equation:

$$Na_4P_2 + 2Na + 4NH_4Br \rightarrow 2NaPH_2 + 4NaBr + 4NH_3$$

Organo-lead compounds in liquid ammonia also react with the salt,[131] and in the general case of R_3PbNa the reaction yields $R_3Pb,PbBr_2$ and RH (R = alkyl group). In other reactions in liquid ammonia, ammonium bromide affects the rate; for example it catalyses a reaction between acetone and liquid ammonia.[132] It may, however, act as an anticatalyst in the reduction of certain organic compounds by sodium in this solvent, examples being the reduction of $1\text{-}C_{10}H_7NO_2$, which is retarded by ammonium bromide, and the reduction of 2-nitrofluorene, which is completely inhibited.[133] Tagged NH_4Br^* has been used to study the complexes K_2PtBr_4 and $K_2[Pt(NO_2)_2Br_2]$.[134] The reaction between 0·05 mole of $p\text{-}MeC_6H_4SO_4Et$ and 0·1 mole of ammonium bromide yields 51·8% of ethyl bromide after 70 min. at 112° to 117°.[135]

Some evidence for the existence of ammonium tribromide has been obtained during measurements[155] of the vapour pressure of ammonium bromide at low temperatures under reduced pressure. Pressure–composition isotherms[156] of the $NH_4Br–NH_3$ system have shown the existence of several ammoniates of ammonium bromide; NH_4Br,NH_3, which has no definite melting point, $NH_4Br,3NH_3$, which is said to melt at 6° (although 8·7° and 13·7° have also been reported), $NH_4Br,6NH_3$, m.p. $-20°$ and $NH_4Br,4NH_3$, the melting point of which has not been reported.

Ammonium bromide acts as a stabilizer of the cubic phase of ammonium nitrate on a mica cleavage surface.[136] The stabilization is effected also by ammonium chloride, but not by the iodide. Ammonium bromide is intermediate between ammonium chloride and ammonium iodide in the catalytic thermal reduction of potassium perchlorate at 525°.[137] Addition of 1 mole-% of ammonium bromide to dry zinc oxide increases the reduction in volume under pressure of the oxide, an effect directly related to the polarizability of the anions in the surface.[138]

The emission spectra of thallium activated with ammonium bromide phosphor have been obtained by using several exciting wave-lengths. The following excited states are proposed to be responsible for the absorption.[139]

Excited state	Electronic Configuration	Wave-lengths of absorption
$1P_1^0$	6*s* 6*p*	258,400
$3P_1^0$	6*s* 6*p*	280,535
$1P_1^0$	6*s* 7*p*	227
$3P_1^0$	6*s* 7*p*	242

Studies[140] of the thermal luminescence and afterglow of $NH_4Br,TlBr$ show that maximum intensity is related to the concentration of the activator. The higher is the degree of isomorphism of the activator and the lattice, the higher is the optimum concentration and the lower is the tendency to concentration quenching, as shown in the systems $NH_4Cl–Tl$ (high isomorphism), $NH_4Br–Tl$ (medium) and $NH_4I–Tl$ (low).[141]

Adsorption of ammonium bromide from aqueous solutions by wood charcoal[142] increases with temperature between 10° and 100° after a slight initial decrease, due to a diminishing surface effect.

APPLICATIONS

Ammonium bromide in amounts up to 0·8 N. affects the characteristics of heat-ripened iodobromide photographic emulsion (4 mole-% AgI), producing larger grain size as the concentration increases, with a maximum at 0·1 N. The grain size then falls to a minimum at 0·2 N and then again rises. When the ammonium bromide is in actual deficiency (e.g. −0·05 N.) the emulsion is useless owing to an opaque fog. With the ammonium bromide in equivalent amount or in but slight excess, the characteristic curve is steep and straight, but with increasing concentration the curve bends over at the top, and finally tends to straighten. The ripening at low temperature subsequent to the first ripening does not affect the statistical grain curve, and at very low concentrations of ammonium bromide there is no increase in the emulsion speed by the low temperature and second ripenings.[143]

The solubility of silver bromide in water is unaffected by the addition of ammonium bromide.[144] Small additions (5 to 10%) of ammonium bromide in the dry distillation of coal are said to decrease the sulphur content of the coke, improving it for metallurgical use.[145] In the preparation of semi-conducting selenium-base material,[146] substances added to increase the conductivity, e.g. tin tetrabromide, may be temporarily stabilized by complexing with ammonium bromide, which, rather surprisingly, also increases the conductivity. Wood treated with ammonium bromide shows a decreased rate of combustion. This treatment was recommended in some countries to economize domestic fuel in the 1939–45 war,[147] and the salt may replace dihydrogen ammonium phosphate in fire-retardant compositions.[148, 149] Flame proofing and fireproofing of cellulose acetate fabric is effected with an aqueous solution containing urea, ammonium bromide and diammonium methyl phosphate.[150] Ammonium bromide is also the foam-producing component in a heat-resistant rubber-like coating containing chloroprene polymer, methyl ethyl ketone, dextrin, zinc oxide and potassium arsenate.[151] Because it can react as an acid, ammonium bromide is used as a component in a solid hair-waving preparation[152] containing calcium thioglycollate. The effect of additions of ammonium bromide to ethylhydroxyethyl cellulose and the determination of flocculating points has been investigated,[153] and it has been mentioned as a possible paper-softening agent.[154]

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SECTION XI

AMMONIUM IODIDE

BY J. D. RICHARDS

PREPARATION

Ammonium iodide is formed by the reaction between iodine and ammonium sulphide[1] according to the equation:

$$2I + (NH_4)_2S \rightarrow 2NH_4I + S$$

and this is the basis of the commercial production of this salt. Another source of ammonium iodide is seaweed.[2] According to a patented process the sea-weed is soaked in water, treated with ammonium oxalate and heated for 2 hr. at 50°; the liquid is poured off, and after treatment with sulphuric acid and the removal of albuminous material, the solution is evaporated. A bacteriostatic preparation,[3] made from urea, formaldehyde and iodine, used as an antiseptic in wounds, contains approximately 2% of ammonium iodide. The salt is also formed by the reaction of carbon tetraiodide and ammonia under pressure between 25° and 150°.[4]

PHYSICAL PROPERTIES OF SOLID AMMONIUM IODIDE

The density of crystallized ammonium iodide has been determined as 2·5142,[5] whilst the melting point[6] is reported as 551 ± 3°, although the accuracy of this determination is affected by dissociation. The refractive index (n_D^{25}) is 1·70070,[5] and the molecular refraction is 0·92 more than that of potassium iodide, owing to hydrogen bond formation.[7] Recent work[8] shows the latent heat of sublimation at 25° to be 43·5 kcal./mole, and the lattice energy[9] in the cæsium chloride type of lattice to be 145·5 kcal./mole by the Born–Mayer method.

Some values at −65° and −80° for the lattice constants and molecular volumes of ammonium iodide and deuteroammonium iodide are given in Table I.

Table I.—Crystallographic Data for Normal and Deuteroammonium Iodide

Substance	Temperature, °C.	Crystal form	Lattice constant	Molecular volume
NH_4I	−65	tetragonal	4·317 A.	48·74 cm.^{3}
,,	−80	tetragonal	4·315 A.	48·70 cm.^{3}
ND_4I	−65	tetragonal	4·313 A.	48·63 cm.^{3}
,,	−80	tetragonal	4·313 A.	48·63 cm.^{3}

X-Ray measurements[13] on the rock salt type crystal by the powder method give the length of the side of the unit face-centred cube of ammonium iodide as 7·244 A. *X*-Ray scattering curves and diffraction patterns have also been recorded.[14–16] The magnetic susceptibility[10] of ammonium iodide is $0{\cdot}413 \times -1 \times 10^{-6}$ c.g.s. units/g.

The heat of hydration,[11] calculated from measurements of heats of solution at infinite or very high dilution and values of lattice energy, is 142 kcal./mole. Experiments[12] on ammonium iodide vapour between 300° and 436° show that the latent heat of evaporation is not a function of temperature, and from the data the molecular heat of evaporation is calculated as 44 kcal. From the same experiments it is concluded that the vapour is completely dissociated at all temperatures up to 400°, that if the substance is perfectly dry practically no decomposition of hydrogen iodide takes place and that there is no tendency for adsorption of ammonium iodide on the glass walls of the vessel.

Transitions

The transition in solid ammonium iodide at low temperatures has been studied by many investigators using various techniques.[17–22] The transition point found by determining specific heats[17] occurs at −17°C. More recent experiments[18] confirm a first-order transition at about −16° from cæsium chloride to sodium chloride structure with a maximum heat capacity at −42°. This is probably due to a change of one or more of the three degrees of freedom of the ammonium ion from torsional to rotational oscillation. Results of these experiments with solid solutions of ammonium iodide in potassium iodide lead to the interpretation of the behaviour on the basis of a change from torsional oscillation to rotation of the ammonium ion at −16°. Other workers[18, 19] found by molecular-volume studies that the transition is homogeneous without hysteresis and that it occurs between −58° and −40°. This is supported by another author[20] who reports −41·65 ± 0·20 as the transition temperature, but Smits and Tollenaar[22] and Shoji[23] showed that transformation in crystal structure takes place continuously.

From considerations based on infra-red spectra[24, 25] phase I of ammonium iodide is believed to have a structure in which one hydrogen bond is formed to the iodide ion with the ammonium ion rotating freely about the bond.

Observations[26] of the variation of dielectric constant with temperature in a single crystal of ammonium iodide show two discontinuities at −13·5° and −44°. A crystal irradiated with *X*-rays turns dark yellow, probably through ionization of the ammonium group, and discontinuities occur at −26° and −52° with a large absorption at 3·3 ev.[26] Absorption measurements[27] with centimetre-waves on ammonium compounds, including ammonium iodide, showed a typical absorption maximum at the same temperature where also either a maximum or a sharp increase of the dielectric constant is observed. Proton magnetic resonance[28] absorption shows line width transitions at −198°, a finding confirmed by other similar work.[29] The heat capacity curves[30] of ammonium iodide measured at various pressures and temperatures show discontinuities, and Table II lists the Curie points given by the discontinuities.

Table II.—Curie Points for Ammonium Iodide

Pressure, kg. cm.$^{-2}$	Temperature, °C.
0	−40·5; −12·98
150	−41·8
280	−44·2
350	−44·9
470	−46·3
550	−47·4
930	−52·5
1250	−56·2

Phase transformations noted during these measurements occur at −13° at 0 kg. cm.$^{-2}$; −1·9° at 150; +12·3° at 300; +33·4° at 600 and 56·7° at 990. At zero pressure the heat of transformation was measured as 227 g.-cal.

The compressibility[31] ($\Delta V/V_0$) at room temperature and solid carbon dioxide temperature under pressure of 50,000 kg. cm.$^{-2}$ is 0·1775 and 0·1702, respectively.

Crystal Growth

The growth of crystals of ammonium iodide has been much studied. The significance of the absolute value of the ionic radius and the appearance of CsCl and NaCl types of crystal, where the radius of the cation is $>1{\cdot}35$ A. and radius of the anion is $>1{\cdot}7$ A., was discussed by Yatsimirsky[32] using ammonium iodide as an example. It has been concluded from polarization of the Raman rays[33] that the ammonium ions are differently oriented in the cubic crystals of ammonium chloride and ammonium iodide; the axis of symmetry of the ammonium tetrahedron is not parallel to the crystallographic axes in these crystals. The change of faces[58] exhibited in simple ionic crystals depends on the degree of supersaturation and the rate of evaporation and is not greatly affected by the presence of impurities. A solution[34] of ammonium iodide near to saturation produces [100] faces and as supersaturation supervenes [100] dendrites form: then at higher degrees of supersaturation [111] faces appear which at maximum values of supersaturation become dendritic. In non-aqueous solutions,[35] e.g. in methyl alcohol, ethyl alcohol, acetone, methyl phenyl ketone and dioxan, slow evaporation produces cubic crystals but by increasing the rate of evaporation octahedra form in all the above solvents except dioxan. Nucleation of ammonium iodide crystals[36] from aqueous solutions occurs in small drops (10–50 micron diameter) of solution if the supersaturation ratio equals or exceeds 1·21. This value corresponds to an interfacial energy between the crystal and solution equal to or greater than 15·4 ergs cm.^{-2}

GROWTH ON MICA SURFACES

On freshly cleaved mica surfaces the supersaturation ratio (S) is related to the 'disregistry' (δ), i.e. the lack of correspondence, between atomic sites on the mica and the atomic sites on [111] plane of ammonium iodide by the equation $\ln S = 3{\cdot}8\delta^2 + 0{\cdot}0059$. The coefficient of disregistry is about 1 to 2 orders of magnitude smaller than that theoretically evaluated, but results agree with Bradley's[37] hypothesis that S for two-dimensional nucleation of ammonium iodide on its own perfect [111] plane is remarkably small, i.e. 1·008 and 1·007 at 46·65° and 30·05°, respectively. The crystal grows with the [111] face parallel to the mica and appears as oriented prisms which can be detected by exposing freshly cleaved mica to a saturated solution of ammonium iodide freed from microcrystals and particulate matter at 30° to 50° and allowed to cool at 1° per hour. Royer,[38–40] from many experiments, reports that the orientation of ammonium iodide is more selective[62] than that of other salts on muscovite, but he found cubic crystals deposited on the surfaces and not octahedra as reported by previous workers. From the orientation of crystals formed on the two faces of a [001] cleavage of muscovite,[39] it was found that the orientation of crystals is determined mainly by that of the last superficial layer, thus providing an extremely sensitive method of studying it. The preferred orientation of the overgrowth noted in some examples of epitaxial crystal growths of ammonium iodide[40] is not solely explicable in terms of the crystal parameters. Yanulov[41] from experiments with [001] mica faces enumerated oriented and unoriented crystals and, from the results, correlated the number of oriented and unoriented intergrowths as a function of the percentage difference of the parameters of both kinds of crystal lattice. For ammonium iodide this difference is only 0·39% and the regular intergrowths are nearly 100%. The orientation of crystals furnishes a means of distinguishing different micas and recognizing decomposition products.[42] The orientation of a crystal growing from a nucleus formed on one side of a cleavage step may differ from that of a crystal seeded on the other side. Despite this a growing crystal of ammonium iodide retains its original orientation and after crystallizing such a step growth is no longer epitaxial.[43]

GROWTH ON OTHER SURFACES

Willems has deposited oriented ammonium iodide at 240° on [010] face of orthoclase and on an $(10\bar{1}0]$ face of quartz,[44] and on cleavage planes of talc and cadmium iodide.[45] Deposits from vapour[46] on to a muscovite cleavage surface have been reported. When ammonium iodide sublimes on to organic films[47] covering freshly cleaved mica surfaces it reorients to tetrahedra by exposure to steam, but sublimation on cellulose acetate films produces no orientation even on exposure to water vapour. Sublimation in air on mica coated with a film of cellulose acetate, formvar or chlorinated rubber 100–200 A. thick shows no initial orientation, but complete tetrahedral orientation occurs on exposure to water vapour. Epitaxial sublimation of various organic crystal deposits[48] on ammonium iodide may produce ionic structures or molecular structures.

CHEMICAL PROPERTIES

An aqueous solution[49] containing 5 g. of ammonium iodide and 5 g. of phosphonium iodide on evaporation to dryness produces large cubic crystals containing 97·9% of ammonium iodide and 1·92% of phosphonium iodide and having a density, 2·525 at 18°, intermediate between the values for the constituents. Pressure–composition isotherms[50] for the binary system NH_3–NH_4I show the presence of ammoniates. In the system NH_4I–KI the transition of ammonium iodide at $-42°$ persists up to 55 mole-% of KI. The first-order transition of pure ammonium iodide at $-7°$ is apparent also in the solid solution with potassium iodide, but between $-10°$ and $-13°$ up to 4 mole-% KI.[51] The molar integral heat of reaction of potassamide, KNH_2, with ammonium iodide has been calculated as 26·5 kcal.[52] Many complexes arise from the reaction of ammonium iodide with various substances. The complex iodide $(NH_4)_2CdI_4$[53] is formed from a mixture of cadmium iodide and ammonium iodide and the formation of complexes is believed to occur on dissolving ammonium iodide in aluminium iodide at 200°.[54] The double salt $PbI_2,NH_4I,2H_2O$[55] is said to form in the system PbI_2–NH_4I–H_2O: mixed crystals are formed in the system NH_4Br–NH_4I.[56] By saturating a concentrated solution of the fluoberyllates with ammonia below 10° and treating the solution with ammonium iodide, complexes of the general formula $M(NH_3)_6BeF_4,NH_4I$ (M = Cu, Ni, Cd, Zn) are formed,[57] the copper salt being blue, the nickel salt violet, and the others colourless.

By heating with ammonium iodide in a quartz crucible barium sulphate and strontium sulphate are converted to the corresponding iodides[58] with yields of 99% and 95% respectively. The determination[59] of stannic oxide in an impure sample may be effected by reaction with ammonium iodide according to the equation

$$SnO_2 + 4NH_4I \rightarrow SnI_4 + 4NH_3 + 2H_2O$$

When the impure oxide is heated with five times its weight of ammonium iodide, the loss in weight is equivalent to the tin oxide and the method is rapid. Lanthanum oxide heated with excess of ammonium iodide at 350° yields lanthanum iodide of about 90% purity.[60] Solutions containing sodium sulphate and ammonium iodide on crystallizing produce crystals of $Na_2SO_4,10H_2O$ with a definite iodine content[61–63] varying from nil to 0·6358% which can be predetermined by adjusting the concentration of the iodide.

Experiments on the exchange reactions of potassium iodoplatinate, K_2PtI_6, with tagged NH_4I^* showed 79 and 89·5% exchanged at 5° and 15°, respectively, after five minutes. The energy of activation of the reaction is 6000 g.-cal./mole.

SYSTEMS CONTAINING AMMONIUM IODIDE

NH_4I–SO_2

In the system NH_4I–SO_2 between $-25°$ and $+25°$ the vapour pressure curve satisfies[65] an equation of the type $\log p = (A/T) + B$: an invariant point, $NH_4I,3SO_2$–NH_4I–solution–vapour, occurs at $-8·8°$.

NH_4I–$Bi(Sb)I_3$–H_2O

The systems NH_4I–SbI_3–H_2O and NH_4I–BiI_3–H_2O show closely analogous ternary phase diagrams[66–68] and the double salts obtained are isomorphous. Other authors report the existence of $NH_4I,BiI_3,2H_2O$, triclinic, $2NH_4I,BiI_3,2H_2O$, triclinic, and $4NH_4I,BiI_3,3H_2O$, quadratic (a special case of a 'dihedral group' which has a square section through the lateral or secondary axis), the latter recrystallizing unchanged from water.[67] The corresponding double salts reported[68] for antimony iodide are black quadratic $4NH_4I,SbI_3,3H_2O$ existing below 75°, bright red unstable $2NH_4I,SbI_3,2H_2O$ and orange-red, fine silky needles obtainable below 20° but very unstable.

NH_4I–HgI_2–H_2O

Systems of mercury halides and ammonium halides have been examined by Belyaev and Mironov.[69–72] Melting diagrams of the iodide systems[69] have been recorded and the liquidus curve[70–72] of NH_4I–HgI_2 shows the incongruent compounds $HgI_2,2NH_4I$ (59 mole-% NH_4I) at 210° and $HgI_2,4NH_4I$ (63 mole-% NH_4I) at 234° and a eutectic at 113° corresponding to 46 mole-% of NH_4I.[72] Isotherms of the electrical conductivity[70] have been determined at 200, 225, 250, 275, 300, 325 and 350°. The 200° isotherm has three sharp minima for 30, 48 and 53 mole-% NH_4I, but only the last corresponds to a compound shown in the melting point diagram. The minima all correspond to maxima of the temperature coefficient of the electrical conductivity and become increasingly shallow with rise in temperature, disappearing at 350°. The cooling curves[71] also indicate the presence of solid solutions between HgI_2 and the 1:2 compound from 0–7 mole-% NH_4I. The melt boils at 388°.

NH_4Cl–NH_4I–H_2O

In the system NH_4Cl–NH_4I–H_2O[74] the solubility of each salt is decreased by addition of the other. No compound or solid solution is formed at 25°, but a ternary eutectic occurs having the composition by weight: NH_4Cl 7·30, NH_4I 56·10, H_2O 36·60%. The effect of ammonium iodide on the solubility of ammonium chloride between 0% and 56·10% NH_4I is shown by the expression

$$x_1 = 28{\cdot}07 - 0{\cdot}4292x_2 + 0{\cdot}001015x_2^2$$

where x_1 = wt.-% NH_4Cl and x_2 = wt.-% NH_4I in the saturated solution. The addition of ammonium bromide to a eutonic solution[75] of the H_2O–NH_4Cl–NH_4I system at 25° causes the displacement of ammonium iodide (the more soluble salt) more readily and to a greater extent than ammonium chloride. The quaternary eutonic point is NH_4I 46·24, NH_4Br 11·12, NH_4Cl 5·83% by weight, and the solubility of ammonium iodide is 10% less and of ammonium chloride 1·5% less than in the eutonic ternary system. It can be seen that the sum of the eutonic solubilities in the quaternary system is practically constant and differs little from the eutonic ternary solution; thus ammonium bromide dissolves at the expense of the water bound by the ammonium chloride and iodide.

Miscellaneous Systems

The ternary system aluminium bromide–xylene–ammonium iodide[76] shows appreciable conductivity owing to complex formation and on electrolysis dense and lustrous aluminium deposits are formed. The addition of ammonium iodide to a solution of aluminium bromide in nitrobenzene increases the specific electrical conductivity[77] and on electrolysis it is probable that ammonia forms at the cathode, but then reacts with the electrolyte so that no deposit or gas evolution occurs. The distribution of ammonium iodide[78] and its mixtures with lithium, sodium and potassium iodides between ethylene glycol and ethyl acetate at 30° has been determined together with stoicheiometric activity coefficients. The reaction between ammonium iodide and butenyl magnesium bromide[79] produces a mixture of butenes. A marked increase in the rate of solution of zinc in aqueous iodine solutions occurs in the presence of increasing concentrations of ammonium iodide, owing to the decrease in the kinematic viscosity.[73]

PROPERTIES OF THE AQUEOUS SOLUTION

Vapour Pressure and Degree of Ionization

In studying concentrated solutions of electrolytes van Ruyven[80] found data for the depression in vapour pressure, degree of ionization and dissociation constant for ammonium iodide, quoted in Table III. Determinations of electrolyte equilibrium and boiling point[81, 82] indicate that the dissociation constant (particularly defined) and degree of hydration for ammonium iodide are 1·97 and 5·5, respectively.

Table III.—Vapour Pressure Depression, Ionization and Dissociation Constant for Ammonium Iodide Solutions

Weight normal concentration	Depression in vapour pressure in mm. at 100°	Degree of ionization at 100°	Dissociation constant at 100°
10	243·5	1·62	—
8	200	1·48	—
6	156	1·39	1·23
5	132·2	1·34	1·40
4	104·5	1·21	1·39
3	78·5	1·13	1·50
2	49·8	0·95	1·23
1	25·1	0·90	—
0·5	12·5	0·86	—

Studies[33] of the freezing points of dilute ammonium salt solutions show an operative factor similar to association which is negligible with other uni-univalent salts. A large electrical potential builds up during the actual freezing of a very dilute solution[84, 85] of ammonium iodide (*ca.* 1×10^{-5} M.). This phenomenon, which also occurs with other solutes, is known as the Workman–Reynolds effect; the sign and magnitude of the potential difference developed are functions of the kind and amounts of contaminants in solution. A potential difference of -109 v. between water and ice has been recorded in a solution of ammonium iodide of specific conductivity 6×10^{-6}. It has been suggested that this potential difference could afford the basis of a new method of microchemical analysis.

Electrolysis

The electrolysis of aqueous ammonium iodide[86] is represented by the fundamental equations:

$$\text{(i)}\ 2NH_4^+ + 2e \rightarrow 2NH_3 + H_2$$

$$\text{(ii)}\ 2I^- \rightarrow 2I + 2e$$

The iodine thus formed reacts with some residual ammonium iodide to give hydrogen iodide and monoiodoamine, according to the equation:

$$2I + NH_4I \rightarrow NH_2I + 2HI$$

The monoiodoamine is unstable and decomposition occurs as follows:

$$4NH_2I \rightarrow 2NH_4I + N_2 + I_2$$

Liberation of oxygen during the electrolysis is due to a side-reaction of hydroxyl ions:

$$2OH^- \rightarrow H_2O + O + 2e$$

and the final products are aqueous ammonia at the cathode, together with iodine and gaseous nitrogen and oxygen at the anode. Theories of conductivity and viscosity of aqueous electrolyte solutions discussed by Pitts[87] introduce the concept of closest approach. Experiments on many salts, which included ammonium iodide, showed agreement between experiment and theory for the conductivity, but experimental values of viscosity deviated from theoretical calculations. Aqueous solutions of ammonium iodide, like those of many other strong electrolytes, have the property of scattering light. Comparison of theoretical and experimental values for dilute solutions of ammonium iodide show only the small differences as characteristic of large anhydrous cations. From results of light scattering measurements the magnetic rotativity, dispersivity and refractivity can be estimated.[88]

PROPERTIES OF NON-AQUEOUS SOLUTIONS

Ammonium iodide[89] is much more soluble in liquid ammonia than in water. A solution of the salt in ammonia exhibits a negative heat of dilution,[91] whilst the osmotic coefficient[92] is the highest of the ammonium halides. Electrolysis of ammonium iodide in ammonia[94] at −70° using 0·001–1·0 amp. yields hydrogen at the cathode, but no iodine is evolved. Some physical constants of the liquid ammonia solution are given in Table IV.

Table IV.—Physical Constants of Solutions of Ammonium Iodide in Liquid Ammonia

Solubility at −35° [90] at 25° [93]	71·3 g. NH_4I/100 c.c. solution 368·59 g. NH_4I/100 g. NH_3
Vapour pressure lowering[92] at 15°	46 mm. in a solution containing 0·290 moles/1000 g. NH_3 192 „ „ „ „ 1·064 „ „
Molar heat effect[91] at −33·4°	20,860 g.-cal. in a solution containing 56·1 moles NH_3/mole of salt
	16,700 „ „ „ „ 74·0 „
	16,750 „ „ „ „ 98·6 „
	14,900 „ „ „ „ 129·5 „
	13,450 „ „ „ „ 372·2 „
	13,350 „ „ „ „ 562·1 „
	13,000 „ „ „ „ 726·5 „

Ammonium iodide is soluble in pyridine[95] in which the conductivity $\Lambda = 95{\cdot}2$ at 25° and the dissociation constant K is $2{\cdot}4 \times 10^{-4}$. Liquid iodine[96] at 130° to 140° also dissolves the salt, as does acetone.[97]

The conductivity of ammonium iodide at 25° in acetone[98] is given in Table V.

Table V.—Conductivity of Ammonium Iodide in Solution in Acetone

Concentration, N × 10^4	Λ
0·4830	160·7
0·8360	160·0
1·635	159·7
2·146	159·3
2·360	157·6
3·313	153·3
5·665	141·6
15·95	112·5

Ammonium iodide is soluble in liquid sulphur dioxide[99] to the extent of 1% at 25° and 12% at 0°. Conductivity measurements on solutions of ammonium iodide in furfural show the high dissociating power of this solvent. The conductivity of this solution increases more rapidly with dilution than with the alkali metal iodides and the Walden equation is not obeyed. The presence of colloidal particles in this solution has been shown.[101]

APPLICATIONS

Industrial Uses

Ammonium iodide has many varied industrial applications. Mixtures of copper, zinc and silver iodides with ammonium iodide in furfural solution can be used for electroplating.[102] Ammonium iodide has been considered as a softening agent for paper.[103] Experiments on the sensitivity of collodion silver iodide wet plates in photography[104] showed that the maximum sensitivity was attained by using a 1:1 ratio of CdI_2:NH_4I in an alcoholic solution containing these salts and potassium bromide. The heat-pack mixture[105] used in coating ferrous metal with chromium and introducing also aluminium and silicon contains 65% Fe–Cr, 0·25% NH_4I, 0·1% I and kaolin. The ammonium iodide removes the oxide skin from the metal and also furnishes at 700° additional iodine to form the volatile chromium compound. Additions of 1 mole-% of ammonium halides affect the reduction of volume under pressure of dry zinc oxide[106] powders; an increase in volume results with ammonium fluoride, but decreases are observed with the other halides, ammonium iodide causing the largest effect. The reduction in volume is directly related to the polarizability of the anions appearing in the surface.

As Catalyst

Ammonium iodide has a catalytic effect on the thermal decomposition[107] of potassium perchlorate. At 525° the rate of evolution of oxygen is too fast to be measured, but at 400° very little oxygen is given off and the mixture is quantitatively converted in a short time into iodate, chlorate and chloride.

In the catalytic phenylation[113] of α-naphthylamine using iodine, hydrogen iodide or ammonium iodide as catalysts, ammonium iodide is found to be the most efficient. The catalytic conversion of hydrocarbons[114] with ammonium iodide has also been reported.

Miscellaneous Uses

Ammonium iodide affects the viscosity of solutions of ethylhydroxyethylcellulose causing the viscosity to pass through a maximum with increasing salt concentration.[112] Atmospheric ice formation by the use of specific substances, among which is ammonium iodide, is discussed by several authors.[108–111]

Ammonium iodide has also been used in admixture with other halides for the defoliation of plants such as cotton,[115] and it has even been suggested[116] that 5–10% should be added in the dry distillation of coal, on the grounds that it decreases the sulphur content of the gas and yields coke suitable for metallurgical use. Thallium can be detected microscopically by the yellow or bluish fluorescence observed when an alkali halide, particularly ammonium iodide, is introduced into the crystal lattice of its salts[117]: ferric iron interferes with this test and must first be reduced or sequestrated as fluoride or phosphate.

The assay of ammonium iodide by oxidation with potassium iodate in acid solution gives irregular results above pH 6·9; this difficulty is avoided[118] by converting the ammonium salt to sodium iodide, which is then treated with potassium iodate under prescribed conditions giving iodine which is then titrated with thiosulphate.

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AMMONIUM TRI-IODIDE

Addition of excess of sulphamic acid, $NH_2SO_2.OH$, to a concentrated solution of ammonium iodide gives on evaporation blue-black deliquescent prismatic crystals of ammonium tri-iodide.[119] The same compound is obtained by the reaction of ammonium iodide with excess of dioxan,[120] and also by heating ammonium iodide solution with a few ml. of aqueous iodine and N-hydroxyphthalonimide,[121] $o\text{-}\overline{C_6H_4CO.N(OH)CO.C}O$. No explosive substance is obtained by melting ammonium iodide and iodine together and testing the cooled substance by percussion,[122] but in the system NH_4I–I a substance with an incongruent melting point at 175° has been shown to be ammonium tri-iodide. In this system, the eutectic is at 10·5% of NH_4I and 88·9°, and at the transition point, 175°, the liquid contains 28·9% of NH_4I in liquid iodine. The liquid saturated with ammonium iodide contains 31·2% of NH_4I at its boiling point, 230°. It was earlier said that the tri-iodide was the only stable polyiodide and its dissociation pressure was reported,[123] but in the system $NH_4I–I–H_2O$,[122] ice, NH_4I, I_2, NH_4I_3, and $NH_4I_3,3H_2O$ occur and probably also NH_4I_5,H_2O, melting incongruently at 9·8°, to give a ternary liquid, solid ammonium iodide and solid iodine. The hydrate $NH_4I_3,3H_2O$ melts incongruently at 7·0°, decomposing into a ternary liquid and solid anhydrous ammonium tri-iodide which is fairly stable and decomposes in air only after several hours.[120, 123] The tri-iodide is very soluble in ethyl alcohol, diethyl ether and benzene, but an aqueous solution dissociates quantitatively to yield ammonium iodide and iodine.[119] The formation of mixed polyhalides of ammonia, NH_4ClI_2, NH_4FI_2 and NH_4BrI_2, has also been reported. The nuclear quadrupole resonance lines[125] of ammonium tri-iodide observed for ^{127}I are 366·23 and 732·13 at 25°, 367·06 and 733·81 at −40° and 368·81 at −196°. *X*-Ray diffraction patterns of the tri-iodide combined with pyridine[126] show the presence of diffuse layer lines superimposed on typical spot diffraction patterns.

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SECTION XII

AMMONIUM CARBONATE

BY K. W. ALLEN

Under this general title are included the three very closely related salts: ammonium carbonate, $(NH_4)_2CO_3$, ammonium bicarbonate, NH_4HCO_3, and ammonium carbamate, NH_2COONH_4. These three individuals are frequently not clearly differentiated, and the term 'ammonium carbonate' is often used to mean a somewhat indefinite mixture of two or all three of them.

NATURAL OCCURRENCE

The natural steam vents (soffioni) at Larderello, Italy, were yielding prior to the 1939–45 war considerable amounts of ammonium carbonate in addition to borax and boric acid. The plant was completely destroyed but was rebuilt on a large scale by 1950, and considerable quantities of ammonium carbonate are now produced by the controlled interaction of the carbon dioxide and the ammonia present in the steam and water.[2–4]

Industrial Production

Since the gases produced by the distillation of coal contain both ammonia and carbon dioxide, neither of which is useful in a fuel gas, the coal-gas industry has long produced ammonium carbonate as a by-product. In order to obtain satisfactory crystallization Wilson passed the gases under a pressure of 3–4 atm. through water.[5, 6] An alternative method uses excess of carbon dioxide from other sources, e.g. producer gas, to ensure the complete removal of the ammonia.[7–9] The ammonia may be concentrated into one part of the gas-liquor and then allowed to react with carbon dioxide.[10–11] The chemical nature of the solid which crystallizes from gas-liquors depends on the ratio of ammonia to carbon dioxide.[12] These processes have been reviewed.[13–15]

A number of processes have been described for producing crystalline ammonium bicarbonate, all of which entail allowing ammonia, carbon dioxide and water to react. Stable, coarse crystals of the bicarbonate free from the other compounds can be formed by cooling, under a pressure of carbon dioxide, solutions which have been saturated at 50–60°C.[16–21] To produce the normal carbonate, $(NH_4)_2CO_3$, the two gases are led into a chamber, the walls of which are wetted with water; the salt is formed as a crust on the walls. This process is best accomplished at temperatures below 60°C.[22–27] Coxon has described a process in which ammonium carbamate is first formed as a dry solid which is then treated with carbon dioxide and a small amount of water to produce dry solid ammonium carbonate.[28–30] Since the 1939–45 war there have been two investigations into the best conditions for preparing ammonium bicarbonate in the saturator process. Klempt showed that the most efficient absorption of carbon dioxide occurred with the highest concentrations of ammonia in the solution and that the process was unaffected by hydrogen sulphide.[31] Brooks reports using the mother liquor from which the bicarbonate had crystallized to absorb carbon dioxide and ammonia gases at temperatures of 30–45°C. The resulting solution was then cooled to 25–27°C. when ammonium bicarbonate crystallized. The mother liquors were returned to the absorber.[32]

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Several other processes have been suggested as possible methods for producing ammonium carbonate, including cracking gas-oil and combining the purified carbon dioxide with catalytically prepared ammonia,[33] catalytic combination of petroleum vapours with oxides of nitrogen,[34] the use of carbon dioxide from the Fischer–Tropsch synthesis, and the use of waste gases from the production of urea.[36] Ammonium carbonate can be separated from the distillate from dry distillation of soya beans,[37] and can be made by heating sugar-beet vinasse with ammonium nitrate and potassium hydroxide.[38]

The commercial products are not very stable, and various methods have been adopted to increase the stability. These include coating the surfaces of the crystals with more stable materials (e.g., sodium bicarbonate, sodium chloride),[39–41] pressing into tablets[42, 43] and adding various organic substances.[44]

Crude ammonium bicarbonate may be purified either by sublimation[45–47] or by recrystallization.[48, 49]

RELATIONSHIP AND SOME PROPERTIES OF AMMONIUM CARBONATE, BICARBONATE AND CARBAMATE

The relationships between ammonium carbonate, ammonium bicarbonate and ammonium carbamate and their various hydrated and mixed crystals are essentially only one part of all the relationships between ammonia, water and carbon dioxide. Indeed some workers have considered them as part of the total relationship of a four component system including carbon, hydrogen, nitrogen and oxygen. There have been three separate extensive investigations which have given rather different results.

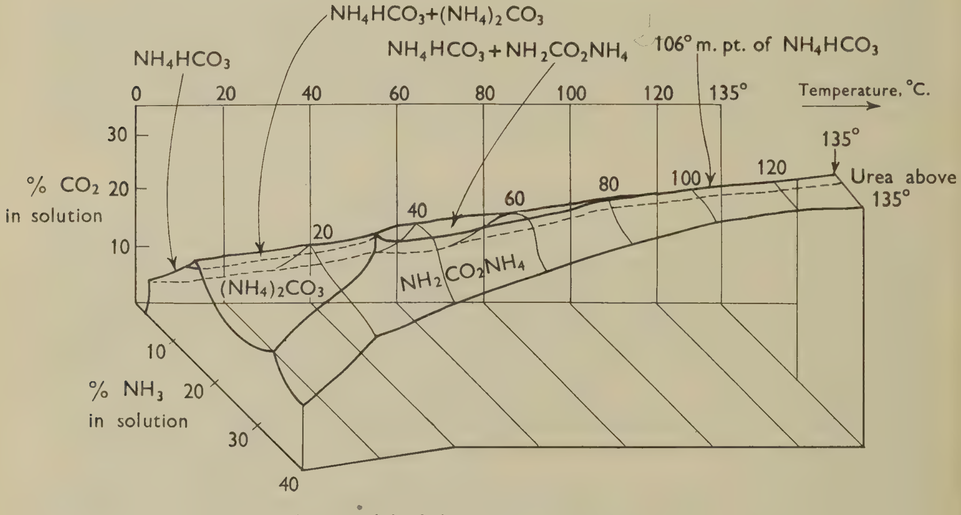

FIG. 1.—Model of the system NH_3–CO_2–H_2O

Terres and his co-workers first measured the partial pressures of ammonia, carbon dioxide and water over solutions of ammonium carbonate of different concentrations over the temperature range 20°C. to 80°C.[50] This work was then extended to give an account of the compounds and their equilibria up to 60°C. Five compounds are reported to exist: ammonium bicarbonate, NH_4HCO_3; ammonium carbonate monohydrate, $(NH_4)_2CO_3,H_2O$; ammonium sesquicarbonate monohydrate, $2NH_4HCO_3,(NH_4)_2CO_3,H_2O$; ammonium carbamate, $NH_2CO_2NH_4$; and a double salt of ammonium bicarbonate and the carbamate, $NH_4HCO_3,NH_2CO_2NH_4$. The normal carbonate and the sesquicarbonate are stable up to about 33°C. while the double salt of bicarbonate-carbamate exists only above this temperature.[51]

Further work extended the investigations up to 135°C. where urea is formed.[52] The solid model representing these results is shown in Fig. 1.

Jänecke and his co-workers studied the whole system: ammonia, water and carbon dioxide,[53, 54] and extended the compositions investigated to embrace urea, dicyanodiamide, *iso*cyanic acid and biuret.[55, 56] Their results differ from those of Terres not only in the general form of the relationships, but also in the compositions of the stable solids formed. Four compounds only are reported; ammonium bicarbonate, ammonium carbonate monohydrate, ammonium carbamate, and anhydrous ammonium sesquicarbonate; the sesquicarbonate monohydrate and the double bicarbonate–carbamate (which Terres reported) are said not to exist. The normal carbonate is stated to be stable up to 43°C. and the sesquicarbonate stable in the range 5°C. to 85°C. Fig. 2 shows the isothermal lines at three different temperatures;

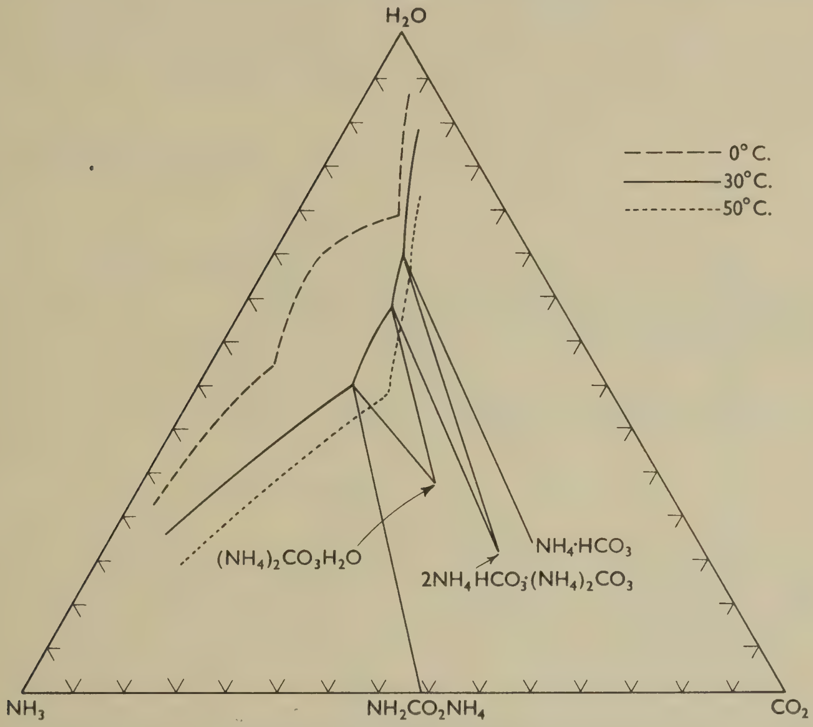

FIG. 2.—Solubilities of ammonium carbonate, bicarbonate, sesquicarbonate and carbamate

The isothermal at 0°C. gives the solubilities of ammonium bicarbonate, ammonium carbonate monohydrate and ammonium carbamate; the isothermal at 30°C. shows the solubilities of ammonium bicarbonate, anhydrous ammonium sesquicarbonate, ammonium carbonate monohydrate and ammonium carbamate; the isothermal at 50°C. gives the solubilities of ammonium bicarbonate, anhydrous ammonium sesquicarbonate and ammonium carbamate.

Guyer and Piechowicz studied the equilibria in solution over the temperature range 20°C. to 50°C.[57] Their results are again different, but tend to confirm and amplify those of Terres rather than those of Jänecke. Five compounds are reported: ammonium bicarbonate, ammonium carbonate monohydrate, ammonium carbamate, ammonium sesquicarbonate monohydrate, and a double salt of the bicarbonate and the carbamate $NH_4HCO_3,NH_2CO_2NH_4$. A further unstable double salt, salt 'S', was observed; it changes into the double bicarbonate–carbamate salt in a few hours. Its composition was not determined. Fig. 3 shows these results in the form of a projection on the composition plane of the three-phase lines together with the isothermal two-phase lines.

The decomposition and vapour pressure of ammonium bicarbonate and its aqueous solutions have been investigated by a number of workers. The vapour pressure of dry ammonium bicarbonate is given by the relationship[58, 59] $\log_{10}P = A - B/T$, where P is pressure in cm. Hg, T is absolute temperature, A is a constant, 11·98, and B is a constant, 3341. The thermal decomposition of ammonium bicarbonate seems to occur in four stages, but these have not been fully investigated.[60, 61]

The vapour pressures of solutions of ammonium bicarbonate have been studied and shown to be functions of the volume of the gas phase associated with the solution, as well as of the temperature and composition.[58, 62–65]

The formation of ammonium carbamate in aqueous solution from carbon dioxide and ammonia has been examined[66, 67] but a final conclusion has not been reached.

The latent heats of sublimation of these compounds at 25°C. have been reported[68] as: ammonium carbonate, $(NH_4)_2CO_3$, 51·2 kcal./g. mol.; ammonium bicarbonate, NH_4HCO_3, 40·8 kcal./g. mol.; ammonium carbamate, $NH_2CO_2NH_4$, 38·1 kcal./g. mol.

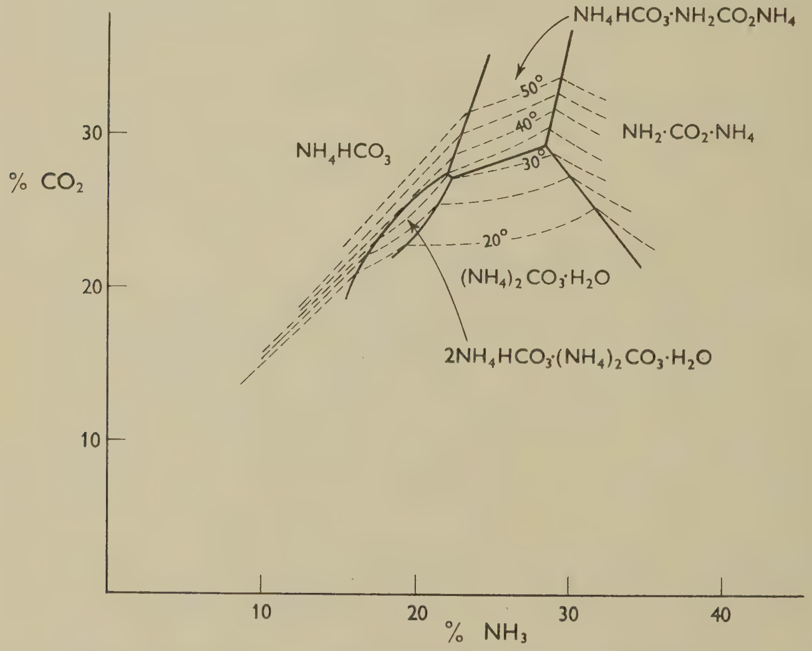

FIG. 3.—Equilibria in the system NH_3–CO_2–H_2O[57]

PROPERTIES OF AMMONIUM CARBONATE AND BICARBONATE

Solubilities

In the course of studies of the ammonia–soda process, much information has been obtained on the solubilities of ammonium carbonate and bicarbonate separately and in the presence of sodium salts. At 15°C. the solubilities are: 62·0 g. of $(NH_4)_2CO_3$ per 100 g. of water,[69, 70] and 18·4 g. of NH_4HCO_3 per 100 g. of water.[71, 72] A number of investigators have reported data for those conditions which are of technical significance for systems involving sodium, ammonium, chlorides and carbonates.[73–76] Some attention has been paid to the possibility of using mirabilite

($Na_2SO_4,10H_2O$) as the raw material for this process, particularly in Japan and in U.S.S.R. Consequently the systems involving sodium, ammonium, sulphate and carbonate have been investigated.[77–88]

Ammonium carbonate has been found to be soluble to the extent of 13·7 g. per 100 g. at 20°C. in 98·2% glycerol[89]; 1·4% in furfural[90]; and less than 0·002 g. per 100 g. at 25°C. in liquid ammonia.[91, 92]

Thermodynamic Properties

A review[93] of the thermodynamic properties of carbonates quotes the following data for ammonium bicarbonate: heat of formation from elements $\Delta H_{298\cdot1} = -203{,}840$ and $-205{,}300$ g.-cal./mole; standard free energy of formation from elements $\Delta F^{\circ}_{298\cdot1} = -159{,}840$ g.-cal./mole; standard entropy $S^{\circ}_{298\cdot1} = -147\cdot6$ e.u.

For the dissociation reactions the following data are given:

(*a*) $NH_4HCO_3 = NH_3 + CO_2 + H_2O(g)$:

$\Delta H = 40{,}680$ g.-cal./mole; $\Delta F^{\circ} = 40{,}680 - 115\cdot16T$ g.-cal./mole; and $\Delta S_{298\cdot1} = 28\cdot3$ e.u.

(*b*) $NH_4HCO_3 = NH_3 + CO_2 + H_2O(l)$:

$\Delta H = 30{,}200$ g.-cal./mole; $\Delta F^{\circ} = 30{,}200 - 86\cdot88T$ g.-cal./mole

Dielectric and Magnetic Properties

It has been stated[94] that ammonium sesquicarbonate belongs to a class of non-polar substances whose dielectric constants decrease regularly with temperature because of diminution of ionic polarization, although no numerical results are quoted in support of the statement.

The magnetic properties of the ammonium ion have been studied and it has been shown to be diamagnetic, the value of the magnetic susceptibility of ammonium carbonate being $-0\cdot443 \times 10^{-6}$ c.g.s. units/g.[95]

Crystal Structure

The crystal structure of ammonium bicarbonate has been examined in various ways by several workers. Measurements of magnetic anisotropy indicate that the planes of different carbonate groups in the unit cells must be considerably inclined to one another.[96, 97] The infra-red absorption spectrum has been measured; the principal lines have the following wave numbers: 649, 697, 832, 947, 985, 1335, 1612 cm.$^{-1}$ These data have been interpreted as corresponding to a planar structure for the carbonate group but with different vibrations due to the different plane in which the hydrogen is situated.[98] A more recent review by Brooks and Alcock gives the atomic co-ordinates for the crystal. Expressed as fractions of the unit-cell edges and taking a centre of symmetry as the origin these are:

carbon	*x*	0·0,	*y*	0·24,	*z*	0·16
oxygen (i)	*x*	−0·03,	*y*	0·19,	*z*	0·03
(ii)	*x*	−0·03,	*y*	0·19,	*z*	0·28
(iii)	*x*	0·06,	*y*	0·35,	*z*	0·17
nitrogen	*x*	0·25,	*y*	0·01,	*z*	0·41

These results are consistent with planar carbonate groups lying on either side of the diad axes with their planes slightly inclined to the *bc* plane of the unit cell, and joined in strings parallel to [*c*] by hydrogen bonds, forming polymeric anions. There is close similarity between the structures of ammonium and sodium bicarbonates, and some relationship to the structure of ammonium hypophosphate.[99] The dielectric properties have been measured on fine crystal powders and the dielectric constant for the bulk crystals calculated by Böttcher's equation giving a value $\bar{\epsilon} = 4\cdot65 \pm 0\cdot07$.

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From this result the molecular polarizability has been calculated giving values of 137·6 A.^{3} and 141·9 A.^{3} depending upon the value taken for the molecular volume. These results indicate that the protons in solid ammonium bicarbonate do not have the freedom which they are believed to have in hydrogen-bonded solids, e.g., ice.[100]

Reactions

The reaction of solutions of ammonium carbonate with fluorine has been shown to yield a variety of products including oxygen, nitrogen, hydrazine, nitrous oxide and nitrite and nitrate ions.[101]

Ammonium bicarbonate may be reduced by hydrogen to yield ammonium formate, most efficiently in the presence of a Raney nickel catalyst at 175°C. and at pressures of the order of 500 atm.[102]

The system ammonia–ammonium carbonate has been suggested as feasible for the concentration of ^{15}N because there is very rapid exchange between the carbamate ion and the other nitrogen species present.[103]

Ammonium carbonate is a constituent of many expectorant medicines and its stability in various forms has been studied for pharmaceutical purposes.[104–106] The loss of ammonia when the dry solid is stored was a source of error in dispensing which could be reduced by employing a 10–12% standardized solution. This retains its concentration for at least a month under ordinary conditions.[107–109] The greater stability of solid ammonium bicarbonate has led to its replacing the carbonate to a considerable extent. Thus while in the British Pharmacopœia, 1932, both were official drugs, in the 1948 and 1953 editions the bicarbonate alone was retained. However, the British Pharmacopœia, 1958, specifies neither salt as an official drug although the carbonate is retained as a reagent.

INDUSTRIAL USES OF AMMONIUM CARBONATE

A considerable variety of uses has been proposed for ammonium carbonate, covering most of the major chemical industries. A first group depends on the formation of gas when the salt is heated and the absence of any residue. Thus it is used to produce porous metals,[110–113] foamed plastic,[114] expanded plaster,[115] solid asphalt-gas emulsions,[116] and as a raising agent in cookery.[117] Akin to this is its use in fire-extinguishing liquids,[118, 119] and perhaps in fire-resistant coatings.[120, 121]

A second major group of uses is in mineralogical processes. Fairly low grade ores that have been treated by leaching with ammonium carbonate solutions include those of copper,[122 123] zinc,[124] nickel,[125] manganese[126] and uranium.[127] The reaction of ammonium carbonate solutions with calcium phosphate as calcined phosphate rock has been investigated as a possible way of obtaining soluble phosphate, but without success.[128–132] In the flotation separation of pyrites it has been found to be advantageous to have small quantities, up to 200 g./ton, of ammonium carbonate present.[133–135]

In corrosion problems ammonium carbonate may either increase or decrease the attack. Several studies have been made of the attack of ammoniacal solutions on copper,[136–139] and it has also been shown that it is the ammonium carbonate present which is primarily responsible for the attack of sea water on concrete.[140] In a number of cases it has been shown that the presence of ammonium carbonate inhibits corrosion.[141–145]

ORGANIC CHEMISTRY OF AMMONIUM CARBONATE

A number of cases of the use of ammonium carbonate as a catalyst for polymerizations have been reported, including polynitroethylene,[146] polyamide[147] and others.[148–150] The effect of ammonium carbonate has been noted in several fermentations where it may either have an accelerating effect[151, 152] or almost completely stop the fermentation.[153] In the preparation of acid amides[154] and amino acids[155] it has been found advantageous to use a mixture of ammonia and ammonium carbonate as the reagent. Hydantoin is prepared by the interaction of glycine nitrile and ammonium carbonate,[156] and substituted hydantoins may be prepared similarly.[157] The reaction of ammonium carbonate with saccharin has been investigated.[158] The formation of urea from ammonium carbonate under various conditions has been studied by several workers[159–162] and several related reactions have been investigated.[163, 164]

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SECTION XIII

AMMONIUM SULPHIDES

BY W. H. LEE AND M. F. C. LADD

PREPARATION

In the preparation of $(NH_4)_2S_x$, or $(NH_4)_2S$, gas-works ammoniacal liquor is heated under such conditions of temperature and pressure as to expel carbon dioxide but not hydrogen sulphide. Distillation and treatment with further hydrogen sulphide yield $(NH_4)_2S$; addition of sulphur gives the polysulphide, $(NH_4)_2S_x$.[1] The separation of ammonia and hydrogen sulphide from industrial gases, and the recovery of ammonium sulphide, have been discussed.[2]

Sulphur may be recovered from the gases produced in the distillation of lignite by passage over activated carbon. The sulphur is used mainly to produce carbon disulphide; ammonium sulphide is prepared from the waste gases of this plant by absorption in ammoniacal liquor.[3]

When coal-gas is passed into ferrous sulphate solution a precipitate of ferrous sulphide may be formed; this is treated with sulphuric acid and the hydrogen sulphide absorbed in aqueous ammonia to give ammonium sulphide.[4]

A semi-industrial scale process for the preparation of $(NH_4)_2S_x$ has been described. A glass tower 33½ in. long and 3½ in. internal diameter, with a central glass inlet tube, is connected to a gas dispensing bulb. The tower is packed with 1 in. Berle saddles, and surrounded by a cooling water spray-coil. The tower contains 28% ammonia solution of density 0·9015, and hydrogen sulphide gas is bubbled through slowly at 20–25°. When saturated, the solution is drained out and one-tenth of its weight of sulphur is stirred in. About one gallon of solution is thus prepared in 2–3 hours, with a high reproducibility of the (NH_4):S ratio, which varied from 2·00:1·58 to 2·00:1·64 in a large number of preparations. Such solutions are suitable for carrying out the Willgerodt reaction (see below).[5]

Solutions obtained by the action of hydrogen sulphide on ammoniacal ethanol contain both NH_4HS and $(NH_4)_2S$, and yield crystals of varying composition. Crystallization followed by rapid washing with ethanol yields nearly pure NH_4HS; the anhydrous compound is best prepared by passing ammonia and hydrogen sulphide alternately into dry diethyl ether. If ether saturated with ammonia is added to the original ethanol solution, crystals of $(NH_4)_2S,EtOH$ are obtained. Attempts to convert NH_4HS into $(NH_4)_2S$ by treatment with more ammoniacal ether yielded only a few cubic crystals, thought[6] to be $(NH_4)_2S$.

Ammonium polysulphide may be prepared by dissolving equivalent amounts of ammonium chloride and sodium sulphide, $Na_2S,9H_2O$, in water, heating the solution with powdered sulphur, adding ammonium hydroxide, and diluting to the required strength. This preparation may be used in qualitative analysis for the separation of Groups IIA and IIB.[7]

Solutions of ammonium sulphide remain colourless on storing if metallic zinc or copper is added to them; the concentration decreases with time, but polysulphide ions are not formed.[8]

PHYSICAL PROPERTIES

Ammonium hydrogen sulphide at room temperature is tetragonal, with $a = 6{\cdot}01$ A. and $c = 4{\cdot}01$ A. The equivalent positions are[9]:

$$\text{N at } 000;\quad \tfrac{1}{2},\tfrac{1}{2},0;\quad \text{S at } \tfrac{1}{2}0u;\quad 0\tfrac{1}{2}\bar{u};\quad u = 0{\cdot}34$$

Reported enthalpies of formation of ammonium sulphides are listed in Table I.[10]

Table I.—Enthalpies of Formation of Some Ammonium Sulphides. Temperature = 298·16°

Compound	State	$\Delta H°_f$
NH_4HS	Crystalline	−38·1 kcal.
	Aqueous	−35·1
$(NH_4)_2S$	Aqueous	−54·1
$(NH_4)_2S_4$	Crystalline	−67·4
	Aqueous	−60·0
$(NH_4)_2S_5$	Crystalline	−68·8
	Aqueous	−61·2

CHEMICAL PROPERTIES

The system ammonia–hydrogen sulphide has been studied at 0°. Two compounds are observed: NH_4HS (m.p. 118°), in equilibrium with solution and vapour at 837 mm. Hg and 0°; and $(NH_4)_2S$, which decomposes at −18°. A eutectic exists consisting of 95% NH_3 and 5% H_2S.[11]

By atmospheric oxidation in the presence of a heated catalyst ammonium sulphide vapour is quantitatively converted into a mixture of ammonium sulphite and ammonium sulphate.[12] Similar oxidation occurs at 100° in air at 10 atm. pressure whereby ammonium sulphate only is obtained.[13]

ANALYSIS

The use of ammonium sulphide solutions in qualitative analysis has been the subject of much investigation. The usual acid decomposition of ammonium sulphide causes the separation of sulphur, which is difficult to remove and may prevent the detection of small amounts of alkaline earth metals in the later Group. If, however, the solution is warmed with slight excess of lead hydroxide and filtered, sulphur is not precipitated; moreover magnesium is no longer partially co-precipitated with the alkaline earth group.[14]

Some organic compounds of iron, e.g. ferratin, do not give a precipitate with a solution of $(NH_4)_2S$, but readily do so with yellow ammonium sulphide.[15]

USES

A solution containing ammonia and hydrogen sulphide in the molar ratio of 2 to 2·7:1 and subsequently saturated with sulphur, is suitable for use as an insecticide or fungicide.[16, 17] A 1 wt.-% solution of ammonium sulphide reduces the rate of corrosion of carbon steel at 75–80° under 100 lb./in.^{2} pressure of carbon dioxide; such conditions obtain in the production of petroleum products.[18] Similarly, corrosion by lubricants and their oxidation may be reduced by 'additives' which are prepared by treating carbonyl compounds with hydrogen sulphide in the presence of ammonium sulphide.[19, 20]

Wax-like substances, which are insoluble in water and alkaline solutions and almost insoluble in many organic solvents, are prepared by treating a mixture of some dihalogenated organic compounds with a polysulphide such as $(NH_4)_2S_x$[21]; similar products obtained from dihalogenated ethers may be mixed with rubber and can be vulcanized.[22] The reaction of formaldehyde with ammonium sulphide yields the compound, $(CH_2)_5S_2N_2$, which may be used as a rubber plasticizer or may be condensed with urea.[23]

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In the Willgerodt reaction an aromatic ketone is converted into an acid amide by aqueous yellow ammonium sulphide.[24] This reaction has been extended to aliphatic carbonyl compounds which undergo reaction without rearrangement.[25] Hydroxyphenyl alkanoic acid esters may be prepared by treating the corresponding ketone with ammonium sulphide, e.g.:

$$p\text{-HO.C}_6\text{H}_4\text{.COOCH}_3 \rightarrow p\text{-HO.C}_6\text{H}_4\text{.CH}_2\text{CONH}_2, \text{ in } 67\% \text{ yield}$$

This reaction is suitable for semi-plant scale operation.[26]

Thioamides[27] and di- and tri-thiols[28] may be prepared from mercaptans in good yield. Carboxamides, which are useful intermediates in the manufacture of pharmaceuticals, surface-active agents and perfumes, may be obtained from alkyl-aralkyl ketones by a modified Willgerodt reaction.[29]

The mechanism, scope and limitations of the Willgerodt reaction have been discussed.[30, 31]

The reduction of aromatic nitro-compounds by ammonium polysulphide is influenced by the properties of the solvent.[32] The reduction of nitroso-phenols generally gives amino-phenols.[33]

The reaction between formaldehyde and ammonium sulphide has been investigated by comparing the products obtained with those formed when alkylammonium sulphides are used.[34]

Ammonium sulphide and acetylene, when passed together over a heated catalyst, form condensation products containing nitrogen and/or sulphur.[35] Thio-amides of higher fatty acids may be prepared from their nitriles by heating these with excess of alcoholic ammonium sulphide at 150–160° under pressure.[36]

In the naphthalene series, reduction by ammonium sulphide occurs preferentially at the β-nitro group; it ceases with mono-reduction.[37]

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SECTION XIV

AMMONIUM SULPHATE

BY F. CALL

PRODUCTION

Ammonium sulphate has been found in a volcanic crater in S. Australia[1] and in the burning shafts at Kladno in Czechoslovakia,[2] but neither of these sources is exploited commercially. The salt is, however, manufactured by the gypsum process (see below) from the ammonium carbonate which occurs naturally in the geysers of Tuscany.[3]

The Direct Process

The insatiable demand for ammonium sulphate as a fertilizer has stimulated interest in its production by a variety of methods and from a wide range of sources. The direct process, in which ammonia is absorbed directly in sulphuric acid, is still widely used. The method is claimed to result in lower production costs, easier plant construction and a saving in capital expenditure as compared with other methods.[4] The efficiency of absorption of ammonia from raw coal gas was found to be 99·17% while the resulting salt after drying had a nitrogen content of 25·57% and an acid content of 0·0113%.[5] Large crystals which do not require subsequent neutralization are said to be produced by injecting atomized liquid acid into ammonia gas.[6] In an earlier variation of this process sulphur dioxide was oxidized to sulphur trioxide in a high-potential arc and the trioxide combined directly with ammonia in an electrostatic field.[7] The direct process can be used to produce a pure salt from the impure waste acid resulting as a by-product from many other processes. Thus the rate of addition of ammonia may be regulated so as to control the pH within desired limits while air is blown into the solution and the temperature is adjusted so as to precipitate metallic impurities.[8, 9] The sulphuric acid of sludges resulting from the acid treatment of lubricating oils can be recovered as pure ammonium sulphate by treating the sludge with anhydrous ammonia[10] or by blowing in ammonia gas and subliming the salt from the mixture.[11] Ammonia may be passed into a solution or suspension of nitre-cake (chiefly bisulphate), at 70°C. to produce a precipitate of the double salt $NaNH_4SO_4$ which is then heated with water to 111°C., when sodium sulphate separates and is filtered off; on cooling to 70°C. ammonium sulphate crystallizes.[12] Alternatively by regulating the concentrations and temperatures anhydrous sodium sulphate and ammonium sulphate may be crystallized alternately, the latter being 95% pure. The acid liquor is much less corrosive than sulphuric acid.[13]

The Gypsum Process

The gypsum process, in which ammonia and carbon dioxide (or ammonium carbonate) react with a suspension of calcium sulphate in water, has proved commercially successful on the large scale.[14] The ammonia may be synthetic[14] or that occurring in raw coal gas[15] or in gas wash liquors,[16] the recoveries of ammonia as sulphate in the two last cases being 52·4 and 65 per cent respectively. It has been claimed that the reaction rate is increased and the occurrence of side reactions suppressed by carbonating the ammonia in a separate vessel from that used for reaction with gypsum.[17] The equilibrium constant of the reaction calculated from the solubility products of calcium sulphate and calcium carbonate is $4{\cdot}82 \times 10^3$, indicating a theoretical yield at 35°C. of 99·95%. It is also deduced from van 't Hoff's isochore that temperature has a negligible effect on the equilibrium. The equilibrium constant found by experiment does not agree, however, with that calculated. The yield with calcium sulphate dihydrate was 85%, with the hemihydrate 92% and with anhydrite 90%. Increasing the concentration of ammonium carbonate increases the yield, but this never attains the theoretical value. With increasing concentration of ammonium sulphate the solubility of calcium sulphate at first increases and then decreases, an effect which is attributed to the formation of a double salt.[18] The rate of reaction is not affected by using gypsum particles finer than those passing a screen 40–70 mesh per cm.[2] but is accelerated by an increase of temperature, equilibrium being reached in 90 min. at 20°C. and in 40 min. at 50°C.[19] Increasing the amount of ammonium carbonate up to 200% excess has no effect on the yield or on the time of reaction, while excess of ammonia reduces the yield. Iron reaction vessels also reduce the yield but lead vessels have no effect.[20] By passing ammonia in countercurrent to a suspension of gypsum in steam and carbon dioxide at pressures of 2–3 atm. and with temperatures ranging from 14° to 120°C., a 40% solution of ammonium sulphate is obtained with utilization of 96·5–98·5% of the gypsum and an ammonia loss of less than 0·2%.[21]

Production from Phosphates and Alunite

'Phospho-gypsum' (resulting from the action of sulphuric acid on a low grade phosphate rock) is satisfactory and reacts faster than natural gypsum. Dilution of carbon dioxide with air reduces the rate of reaction.[22] Gypsum-containing marls are satisfactory,[23] as are mixtures of gypsum with clay[20] or blast furnace slag,[24] with the additional advantage that the residue can be converted into Portland cement. Ammonia and carbon dioxide also react with a solution of magnesium sulphate.[25] A purer product is said to be obtained if the reaction is effected in two stages[26]:

$$MgSO_4 + 2(NH_4)_2CO_3 \rightarrow (NH_4)_2SO_4 + (NH_4)_2CO_3MgCO_3{,}4H_2O$$

the double salt being filtered off and treated with more magnesium sulphate;

$$(NH_4)_2CO_3MgCO_3{,}4H_2O + MgSO_4 \rightarrow (NH_4)_2SO_4 + 2MgCO_3{,}3H_2O$$

A study of the reaction scheme:

$$\begin{aligned} &MSO_4 + 2NH_4OH \rightarrow M(OH)_2 + (NH_4)_2SO_4 \\ &MO + O \rightarrow MO_2 \\ &MO_2 + SO_2 \rightarrow MSO_4 \end{aligned}$$

led to the conclusion that chromium is the best metal for the purpose, but the method does not appear to have been applied commercially.[27] Waste ferrous sulphate solutions, e.g., from pickling operations, can be used for the preparation of ammonium sulphate by treating them with ammonia[28] or ammonium carbonate[29] and passing a current of air to oxidize the ferrous hydroxide to ferric hydroxide. Ammonium sulphate crystallizes in 86% yield when alunite, $K_2Al_6(OH)_{13}(SO_4)_4$, is calcined at 600°C. and treated with aqueous ammonia.[30] Alternatively the calcined alunite may be treated first with calcium hydroxide, ammonia and carbon dioxide being passed into the resulting suspension of calcium sulphate; ammonium sulphate is then obtained in 92–98% yield.[31]

Production from Sodium Sulphate (Mirabilite)

Extensive study has been devoted to the production of ammonium sulphate from sodium sulphate, which occurs in very large deposits in Russia as mirabilite, by means of the reaction:

$$Na_2SO_4 + 2NH_4HCO_3 \rightarrow (NH_4)_2SO_4 + 2NaHCO_3$$

These investigations have covered the solubility relationships of the various components,[32–34] the relation between the vapour pressures of the volatile components and the composition of the solution and the kinetics of carbonation.[34] It is found that the optimum reaction conditions required are: an equimolecular ratio of reactants, saturated sodium sulphate solution at 34°C. and high carbon dioxide pressures. Conversion of sulphate decreases with increasing ammonia concentration and with decreasing ammonium carbonate concentration. The conversion is 65% after 24 hr. at 30°C. with a pressure of carbon dioxide at 5 atm., while equilibrium is reached with 51% conversion after 16 hr. under a pressure of 1·14 atm.[35] Maximum utilization of raw materials and the highest concentration of ammonium sulphate are obtained by freezing out the sodium bicarbonate at -15°C. The yield of ammonium sulphate could be increased by neutralizing with sulphuric acid the ammonium carbonate remaining in the frozen-out solution.[36] Commercial processes have been developed for use with a soda column[37] and with a Honigmann carbonator[38] while the sodium sulphate can be in solution or in suspension.[39]

Production from Sulphur Dioxide and Ammonia

Since sulphur dioxide is a common by-product in industrial processes, there is much interest in the direct reaction of this gas with ammonia and subsequent oxidation of the resulting sulphite to ammonium sulphate. The cost of production may be substantially lower than for other processes.[40] The rate of oxidation of ammonium sulphite and bisulphite solutions by atmospheric oxygen decreases markedly with increasing concentration of the solution. Temperature has only a slight effect on the rate of oxidation of sulphite solutions but a considerable effect on that of bisulphite solutions up to 50°C., above which temperature thermal decomposition to ammonium sulphite and sulphur dioxide begins to predominate. The oxidation is found to be unimolecular with respect to oxygen.[41] The oxidation of ammonium sulphite solutions is said to occur most rapidly at 70°C.,[42] at which temperature there is some dissociation into ammonia and sulphur dioxide.[43] The rate of reaction may be speeded up by atomizing the oxygen or air into the liquid under 15 atm. pressure.[44] When heated to 200°C. under pressure ammonium sulphite undergoes autoxidation to yield a mixture of ammonium sulphate and ammonium sulphide; the latter may be removed as ammonia and hydrogen sulphide.[45] Oxidation of solid ammonium sulphite by air is very slow and even at 60–70°C. an apparent equilibrium is reached in 2–3 hr. with only 30% conversion to ammonium sulphate.[46] Although many metal salts catalyse the oxidation, the catalytic effect of cobalt salts is outstanding[47] and is attributed to the formation of a soluble cobalt sulphite–ammonia complex. The rate of oxidation is maximal at pH 8·4–8·6 and a concentration of ammonium sulphite of 70 g. per litre.[43] Excess of ammonia,[48] hydrogen or hydroxide ions, metal salts or sulphides[47] have a negative catalytic effect. At 20°C. the spontaneous oxidation of aqueous ammonium sulphite increases linearly with time, whereas oxidation in the presence of cobalt nitrate is at first very rapid and then decreases to a linear rate about twice that of the uncatalysed oxidation. Under high pressures of oxygen with cobalt nitrate present oxidation of ammonium sulphite is complete in 10–60 minutes.[48] Other catalysts which have been successfully employed include silica gel,[46, 49] oxides of nitrogen[50] and sulphur.[51] Oxidation of ammonium sulphite has also been effected by electrolysis in the presence of a chloride[52] or by allowing the atomic oxygen produced at the anode to oxidize the sulphite ion.[53] The efficiency of oxidation is reduced by decreasing either the pH value or the concentration of sulphite or by increasing the current density. Ammonium sulphate has been produced by passing sulphur dioxide and air through an electric arc[54] or over active silica heated to 470°C.,[55] mixing the effluent gases with ammonia gas and separating the resulting ammonium sulphate and sulphite in an electrostatic precipitator. Coke-oven gas containing ammonia and hydrogen sulphide

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yields ammonium sulphate directly when passed through 45% hydrogen peroxide, 82·5% of the peroxide being utilized.[56]

When a mixture of ammonium sulphite and bisulphite is heated in an autoclave below 200°C. ammonium thiosulphate, polythionates and sulphate are formed. Above 200°C. the two former salts decompose with deposition of sulphur, and at 300°C. the yield of ammonium sulphate becomes 95–99%, but this yield falls sharply with dilution of the solution.[57] It has been stated, however, that decomposition into sulphate and sulphur begins at 150–160°C., the reaction being rapid and producing a dangerous rise of pressure.[58] Selenium has been found to be a useful catalyst for this reaction, but sulphur is less satisfactory.[59] In the presence of ammonium sulphate and free sulphuric acid, ammonium bisulphite reacts with ammonium thiosulphate, ammonium trithionate or higher polythionates under the influence of pressure and heat to form ammonium sulphate and free sulphur,[60, 61] and by adjusting the proportion of thiosulphate in the feed solution the process can be run continuously. If this proportion is incorrect, either ammonia or sulphuric acid will accumulate in the reaction vessel. The thiosulphate may be produced by treating a portion of the ammonium bisulphite solution with ammonia and sulphur in a ball mill.[62] Ammonium thiosulphate is a by-product of the Katasulf process of coal-gas treatment and may be converted into ammonium sulphate by reaction with sulphuric acid at 90°C.,[63] no sulphur dioxide being liberated if the amount of sulphuric acid is carefully controlled.[64] Alternatively the ammonium thiosulphate may be treated with sulphur dioxide in the molecular proportions of 2:1 whereby on heating above 40–50°C. ammonium sulphate and sulphur are formed.[58] The same products are obtained when coke-oven gases containing ammonia and hydrogen are washed with a solution of ammonium thiosulphate containing an organic oxygen carrier such as hydroxybenzene at temperatures above 80°C.[65] Oxidation of ammonium thiosulphate by oxygen under pressure yields firstly ammonium sulphate and ammonium trithionate, the latter being further oxidized to more sulphate and ammonium sulphamate which can be removed by hydrolysis.[66] Ammonium thiocyanate which is formed during the processing of coal gas may be converted to ammonium sulphate by hydrolysis with sulphuric acid,[67, 68] but it is said that this reaction is very corrosive to plant material and that a better method is to heat the thiocyanate with ammonium bisulphite, ammonium thiosulphate or ammonium trithionate when it is converted quantitatively into ammonium sulphate, sulphur and carbon dioxide.[69]

Production from Coal

The most important single source of ammonium sulphate is the distillation of coal and much effort has been devoted to improving the yield and the efficiency. A study of the heat balance for manufacture by various methods indicates that the direct process may show a heat surplus or deficit depending on the concentration of ammonia in the gas; in the semi-direct process (after prior removal of tar) external heat is usually required, while in the indirect process the heat of reaction is sufficient to cover requirements.[70, 71] The yield of ammonium sulphate depends on the temperature of carbonization of the coal, falling off rapidly at temperatures below 800°C.,[72] and more gradually as the temperature is raised above this figure.[73] Thus the yield in pounds per ton of coal ranged from 22·5 to 35·9 at 800°C., from 19·6 to 30·1 at 900°C. and from 15·5 to 27·4 at 1000°C.[74] A method of low temperature carbonization has been developed which is claimed to give yields of 88–110 lb. per ton.[75] Dry distillation of coal with calcium oxide is also claimed to increase the yield with, however, adverse effects on the coking properties.[76] Gasification of peat has been found to yield 55·44 lb. of ammonium sulphate per ton, a recovery of 70%, but after treatment of the peat with hydrogen peroxide under high pressure yields as high as 176 lb. per ton have been obtained.[78, 79] Dry distillation of oil shale has given yields of ammonium sulphate of 27·6[80] and 60 lb.[81] per ton. A laboratory method has been developed for determining the available yield.[82]

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Miscellaneous Sources

Other sources of ammonium sulphate which have been proposed are spent wash from molasses,[83] sugar beet molasses,[84, 85] spent ion-exchanger regenerants used in sugar beet processing,[86] vinasse[87] and cyanide sludge.[88]

Ion exchangers are beginning to be used in the manufacture of ammonium sulphate. Thus the ammonia formed in urine by the action of urease was removed by passage through a base exchanger and subsequent treatment with sulphuric acid gave ammonium sulphate in a yield of 80% based on the original nitrogen content of the urine.[89] Cation exchangers have been used to absorb ammonia from coal-gas wash liquor[90] and from waste cuprammonium liquor.[91] Ammonium carbonate solution has been passed through a sodium-saturated resin, the adsorbed ammonia being removed as ammonium sulphate by means of sulphuric acid[92] or sodium sulphate solution.[93]

STORAGE AND TRANSPORT

For storage and transport purposes it is desirable that ammonium sulphate should consist of non-caking, coarse-grained crystals, and much attention has been devoted to the production of a uniform product of the required standard. The shape and size of the crystals are influenced by both physical and chemical factors.[94] Thus the homogeneity and degree of supersaturation of the solution, the time of growth of the crystals and the number of nuclei must all be carefully controlled, and the design of the saturator plays an important part.[95–99] Although such impurities as pyridine, tar acids, phenol and arsenic appear to have no effect on the form of the crystals, the presence of ferric iron, and to a lesser degree of chromium or aluminium salts, causes the separation of very fine elongated crystals. Ferrous iron and the lower valence forms of manganese or cobalt salts have the opposite effect, the crystals being large and stubby.[100–104] It has in fact been proposed that ferrous iron be maintained at a concentration of 1 g. per kg. of solution to improve the crystal form.[102] Control of the concentration of ferric salts has been achieved by the addition of phosphoric acid or phosphates,[103, 105] of ammonia[100, 105] or of oxalic acid and magnesium sulphate.[107, 108] Crystal size is dependent also on the concentration of acid in the crystallization bath, the size increasing to a maximum at a sulphuric acid content of 9–15 g. per l.[103, 106] The concentration of acid may be automatically controlled by means of an external conductivity cell and a relay.[109]

The caking of ammonium sulphate has been variously ascribed to the presence on the crystals of a film of moisture,[110, 111] of saturated solution,[112] of dilute sulphuric acid[113] or of pyridine sulphate.[114, 115] The importance of free sulphuric acid has been disputed and it has been shown that even neutral ammonium sulphate absorbs water indefinitely on exposure to a damp atmosphere, subsequently caking on drying.[111] Proposals to avoid caking have included careful control of storage conditions,[110] dusting with kieselguhr,[110] and treatment with ammonia gas or solution.[114] Ammonium sulphate contaminated with a benzene-soluble impurity has been found to be difficult to dissolve in water.[116]

PURIFICATION

Ammonium sulphate has been purified for use in chemical analysis by repeated crystallization from dilute sulphuric acid solution.[117] By treating the solution with milk of lime at 90°C. so as to maintain the pH value between 7 and 8 for 2 hr., it is claimed that the pyridine content is reduced to 0·001%.[118] The salt may be purified from alkali or alkaline-earth metal salts by sublimation at 380–400°C.[119] Phenols may be removed by adsorption on active charcoal.[120] By adding creosote oil emulsified in water with soap to the saturator it is claimed that discoloring impurities including arsenic trisulphide are brought to the surface as a heavy scum.[121] Discoloration by impurities such as ferrocyanide may be prevented by careful control of

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the specific gravity of the solution in the saturator[122] or by precipitating metal salts by neutralization before centrifuging off the crystals.[123, 124] It is claimed that quinquevalent arsenic if present in sufficient concentration precipitates metallic impurities.[125]

Although ammonium sulphate prepared by the gypsum process is quite neutral,[126] that made by the direct method may contain free acid. It is possible to neutralize the acid completely in the saturator,[127] but there is then a danger of the formation of Prussian Blue[128] and it is usual to neutralize the salt by gaseous or aqueous ammonia.[128–131] The minimum acid content attainable by washing alone appears to be 0·2%.[129] Neutralization by solid ammonium carbonate has been proposed[132] but appears to be less satisfactory.[133]

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PHYSICAL PROPERTIES

Crystal Structure

Ammonium sulphate crystallizes in the orthorhombic system with four molecules per unit cell. The space group is V_h^{16} and the dimensions of the unit cell are $a = 5{\cdot}98$, $b = 10{\cdot}62$ and $c = 7{\cdot}78$ A.[1] The salt is isomorphous with the sulphates of cæsium,[1] potassium and rubidium[2] and with the fluoberyllates of these metals.[3, 4] The crystal shape depends markedly on the composition of the original solution. Thus at lower pH values or in the presence of ferric, aluminium or chromium ions the prisms are elongated and reduced in size.[5] Certain dyes also cause modification of the crystal habit, the effect being most marked in the [001] direction.[6] Crystals produced in the presence of sulphuric acid increase in size with increasing acid concentration up to 9–15 g. per l. and decrease thereafter.[7] Sodium metaphosphate may also be used with sulphuric acid to increase the crystal size.[8] Ammonium chloride and nitrate delay the onset of crystallization and the crystals produced may be plate-like or acicular.[7] *X*-Ray investigation of mixed crystals of ammonium and potassium sulphates suggests that substitution in the lattice is purely random.[9] The bulk density of ammonium sulphate may vary between 0·64 and 1·04 depending on the size and shape of the crystals.[10] The sulphate ion and the crystal force field do not possess tetrahedral symmetry and the changes produced in the force constants by the electric fields have been calculated, along with the accompanying perturbations of the frequencies of the sulphate ion tetrahedron, for ammonium sulphate.[11]

Melting Point, Thermal Conductivity and Specific Heat

When heated, ammonium sulphate evolves water and ammonia so that it is impossible to determine a true melting point.[12] The end product is said to be ammonium pyrosulphate which has a melting point of 513°C.[13]; this temperature has previously been quoted as the melting point of the sulphate (Mellor, II, 699). The thermal conductivity of ammonium sulphate[14] is 0·230 g.-cal. mol.$^{-1}$ hr.$^{-1}$ deg.$^{-1}$ A thermal transition found to occur at $-49{\cdot}71 \pm 0{\cdot}10$°C. and ascribed to rotation of the ammonium ion,[15, 16] is clearly shown by the specific heat curve which has been determined at various temperatures between -90° and $+10$°C. The specific heat increases steadily with temperature from a value of 47·30 g.-cal. mol.$^{-1}$ at -90°C. to 69·15 g.-cal. mol.$^{-1}$ at -60°C. and then rises sharply to a peak of 208·25 g.-cal. mol.$^{-1}$ at -50°C., falls abruptly to 60·43 g.-cal. mol.$^{-1}$ at -49°C. and thereafter increases regularly with temperature.[17] More precise measurements showed this peak to occur at 223·4°K. ($-49{\cdot}6$°C.) and gave a total heat absorption at this temperature of 22,219 g.-cal. mol.$^{-1}$ from which it is calculated that the molecule has $4{\cdot}0 \pm 0{\cdot}4$ entropy units in excess of normal.[18] The specific heat of solid deuteroammonium sulphate, $(ND_4)_2SO_4$, measured between -180° and $+20$°C. is 5–6 g.-cal. mol.$^{-1}$ greater than that of ammonium sulphate at the same temperature and shows the same discontinuity at $-49{\cdot}5$°C. The heats of transition are 210 and 215 g.-cal. g. ion^{-1} for ammonium and deuteroammonium sulphate respectively.[19] Thermal analysis showed that this transition, at $-48{\cdot}5$° C., occurs at approximately the same temperature in mixed crystals of ammonium sulphate and ammonium nitrate and in the double salts $(NH_4)_2SO_4,Na_2SO_4$ and $(NH_4)_2SO_4,NaSO_4,4H_2O$, but not at all in the double salt $(NH_4)_2SO_4,2NH_4NO_3$.[20, 21] The specific heat of ammonium sulphate between 50° and 150°K, is given with an error of less than 0·5% by the expression

$$C_p = D(121{\cdot}7/T) + 2E(201/T) + 4E(472/T) + 8E(1090/T)$$

where *D* is the Debye function and *E* the Einstein function.[18] Over the temperature range 298–440°K. the specific heat is given[22] within 0·8% by the equation

$$C_p = 24{\cdot}77 + 67{\cdot}2 \times 10^{-3}T$$

the values at 276·4° and 296·1°K. being 43.55 and 44·80 g.-cal. mol.$^{-1}$

Thermodynamic Functions

The heat content of solid ammonium sulphate in excess of the value at 298·16°K. has been determined at various temperatures up to 600°K. and found to accord with the equation:

$$H_T - H_{298\cdot16} = 24\cdot77T + 0\cdot0336T^2 + 10\cdot372 \text{ g.-cal. mol.}^{-1}$$

with an accuracy of 0·8%. From these data the excess entropies and free energies over the values at 298·16°K. have been calculated at various temperatures.[23] The entropy of the solid salt[22] is 4·55 at 30·12°K. and 52·6 at 298·16°K. At 298·16°K. the heat of formation from the elements[18] in g.-cal. mol.$^{-1}$, $\Delta H_{298\cdot16}$, is $-281{,}740 \pm 480$ g.-cal. mol.$^{-1}$ with an entropy change $\Delta S_{298\cdot16}$ of $-223\cdot8 \pm 0\cdot3$ e.u., from which the free energy of formation is calculated as $-215{,}010 \pm 490$ g.-cal. mol.$^{-1}$ The heat of formation from gaseous ammonia and 96·57% sulphuric acid was found to be 63·89 kg.-cal.mol.$^{-1}$, from which the heats of formation from 98·5 and 100% acid are calculated as 64·77 and 65·44 kg.-cal. mol.$^{-1}$ respectively.[24] The molal heat of solution[25] is -454 ± 6 g.-cal. mol.$^{-1}$ The heat of hydration[26] is 391 kg.-cal. mol.$^{-1}$, and the most probable values of the separate heats of hydration are for the ammonium ion 79 and for the sulphate ion 243 kg.-cal. g. ion^{-1}.

Solubility

The solubility of ammonium sulphate in water together with the density of the saturated solution have been determined at various temperatures from the cryohydric point, −18·5°C., to the boiling point,[27] and the results are given in Table I. Solubilities can be calculated to a close approximation from the expression $S = 41\cdot22 + 0\cdot09t$.

Table I.—Solubility in Water and Density of Saturated Solutions of Ammonium Sulphate at Various Temperatures

Temperature, °C.	Solubility, g./100 g. of water	Density, d_4^t
−18·5	39·75	—
−11·52	40·42	—
−6·55	40·59	—
0	41·22	1·242
5	41·65	1·242
10	42·11	1·243
15	42·52	1·244
20	43·00	1·245
25	43·47	1·246
30	43·87	1·247
40	44·80	1·248
50	45·75	1·248
60	46·64	1·249
70	47·54	1·250
80	48·47	1·251
90	49·44	1·253
100	50·42	1·257
108·5	51·53	—

Solubilities have also been determined[28] (g./100 g. water) at temperatures above 100°C., and these increase regularly from 54.5 at 138°C. to 79·6 at 410°C. Nomograms have been published[29] for the preparation of ammonium sulphate solutions of known degrees of saturation at 0° and 20°C. By cooling solutions with vigorous agitation until crystallization occurred it is claimed that supersolubility was produced,[30] the solubility being 3·78–5·40% higher than normal values in the temperature range 18·5–42·9°C. The solubility of ammonium sulphate in ammonium hydroxide solutions at 0°C.[31] is given in Table II.

Table II.—Solubility of Ammonium Sulphate in Ammonia Solutions at 0°C.

Ammonia, g./100 g.	0	10	20	30	40	50	60	70	80
Ammonium sulphate, g./100 g.	70·6	54·0	36·3	20·2	12·1	8·3	5·9	4·3	3·1

Solubilities in ammonia have been determined also[32] at various temperatures in the range 5–35°C. Ammonium sulphate is stated to be more soluble in sulphuric acid solutions than in water, and the specific gravity of saturated ammonium sulphate solutions containing $X\%$ of sulphuric acid is given[33] by the equation: $\text{s.g.} = 1{\cdot}243 + 0{\cdot}0065X$. 100 c.c. of a saturated solution of ammonium sulphate at 18° dissolves only 6·4 g. of sodium nitrate and 0·4 g. of sodium chloride.[34] The effect of ammonium sulphate on the solubility of lead sulphate in water has been determined at 18°C. The solubility declines steadily from 34 mg./l. with no other salt present to 3·25 mg./l. in 0·0189 molar ammonium sulphate, but thereafter increases to 15·72 mg./l. in 1·13 molar ammonium sulphate.[35, 36] Studies have also been made of the effect of ammonium sulphate on the solubility of magnesium ammonium phosphate,[37] calcium oxalate,[38] ammonium persulphate,[39] boric acid[40] and nicotine.[41]

Properties of Ammonium Sulphate Solutions

DENSITY

The density of saturated aqueous solutions of ammonium sulphate at various temperatures is given in Table I, while the density at 25°C. of solutions of various concentrations appears in Table III below, concentrations being expressed in molalities[42] and in normalities[43]; the latter publication gives also the specific volumes of solutions of various normalities.

Table III.—Density at 25°C. of Solutions of Ammonium Sulphate

Molality	Density d_4^{25}	Normality	Density d_4^{25}
1·70760	1·05560	0·489	1·0158
3·99962	1·11773	0·979	1·0336
5·81062	1·15708	1·958	1·0682
8·02032	1·19670	2·936	1·1000
10·6389	1·23426	3·915	1·1302
		4·894	1·1593
		5·873	1·1851
		6·851	1·2119
		7·830	1·2358

The density at 0°C. of solutions containing 5·146 and 38·25 g. per 100 g. is 1·0355 and 1·2321, respectively.[44]

ACTIVITY

The activities of aqueous ammonium sulphate solutions have been determined at 25°C. by the isopiestic method[45] and the results are given in Table IV. It is stated that concentrated solutions behave like uni-univalent electrolytes owing to the extensive formation of the ion pair $NH_4SO_4^-$.

Table IV.—Activity Coefficient of Ammonium Sulphate Solutions at 25°C.

Molality	Activity coefficient	Molality	Activity coefficient
0·1	0·439	0·9	0·205
0·2	0·356	1·0	0·196
0·3	0·311	1·2	0·182
0·4	0·280	2·0	0·149
0·5	0·257	3·0	0·130
0·6	0·240	4·0	0·120
0·7	0·226	5·0	0·115
0·8	0·214	5·84	0·112

The activity of water in supersaturated solutions of ammonium sulphate has been determined[46] at temperatures from 35° to 50°C. by measuring the vapour pressure of the solution. The activity in a solution of 78 g. of salt in 100 g. of water is at 35°C. 0·790. The activity falls to a minimum of 0·787 at 45°C. and rises again to 0·796 at 50°C. Determinations of the activity coefficients of sulphuric acid in aqueous solutions of ammonium sulphate at 25°C.[47] show that the effect of the ammonium salt is intermediate between those of sodium sulphate and potassium sulphate. The acidity function of sulphuric acid was found to decrease with increasing concentration of ammonium sulphate,[48] the effect again lying between those of sodium sulphate and potassium sulphate. Precise determinations have been made of the freezing point depression of ammonium sulphate solutions and the results disclose the existence of an unexplained factor similar in its effect to that of association.

DISSOCIATION

The degree of dissociation of ammonium sulphate in solution has been calculated[50] from conductivity data and the results are given in Table V.

Table V.—Dissociation of Ammonium Sulphate in Solution

Molarity	Dissociation constant α	Ionic strength μ	Log K'	Log K
0·005	0·072	0·01428	−0·906	−1·137
0·01	0·109	0·02782	−0·811	−1·131
0·025	0·157	0·06715	−0·607	−1·087
0·05	0·192	0·1308	−0·420	−1·070
0·10	0·233	0·2534	−0·235	−1·100

In this table α is the fraction of the bivalent radical existing as the intermediate ion, K' is the dissociation constant of the second stage of dissociation and K is the dissociation constant of the Debye–Hückel equation.

Because of their smaller degree of dissociation, solutions of ammonium sulphate exhibit higher pH values than other ammonium salts. Thus the pH of solutions in very pure carbon dioxide-free water[51–53] increased from 5·63 at a dilution of 10 litres per g.-equivalent to 6·55 at a dilution of 1000 litres and extrapolated to 7·16 at infinite dilution. Corrections have been calculated for the effect of various concentrations of ammonium sulphate on the pH values of various proteins.[54]

It has been estimated[26] from heat of hydration data that eight molecules of water are associated with each ion and that the effective radius of the water molecules in the hydrate envelope is 1·91 A. for the ammonium ion and 2·05 A. for the sulphate ion.

VISCOSITY AND SURFACE TENSION

The viscosity of ammonium sulphate solutions has been reviewed and experimental values of the constants of the Onsager–Fuoss equation compared with theoretical values.[55] The coefficient of inner friction and the fluidity have been determined for solutions at 25°C. from 0·489 to 7·830 normal.[43] The inner friction relative to water, ϕ, has been determined for aqueous solutions of various concentrations at 20°, 40°, 60° and 80°C. and also for solutions containing equimolar concentrations of sulphuric acid. The values of the relative inner friction ϕ at 20°C. for solutions 0·4375, 0·875, 1·75 and 3·5 molar are respectively 0·01089, 0·01196, 0·01455 and 0·2394.[56] The relative inner friction and density have also been determined[57] for solutions 1·75 molar in ammonium sulphate containing various concentrations of sulphuric acid from 0 to 2·75 molar at 20°C., 40°, 60° and 80°C.

The surface tension[58] of ammonium sulphate solutions at 20°C. is given in Table VI.

Table VI.—Surface Tension of Ammonium Sulphate Solutions

Concentration, molar	3·500	1·750	0·875	0·4375
Surface tension, dynes per cm.	82·73	76·58	74·93	73·75

VAPOUR PRESSURE

The vapour pressure of saturated solutions of ammonium sulphate at various temperatures[59] is given in Table VII.

Table VII.—Vapour Pressure of Saturated Ammonium Sulphate Solutions

Temperature, °C.	19	20	21	22	23	24
Vapour pressure, mm. Hg	13·30	14·20	15·12	16·09	17·11	18·06
Temperature, °C.	25	26	27	28	29	30
Vapour pressure, mm. Hg	19·26	20·42	21·67	23·01	24·42	25·82

At 0°C. a saturated solution of ammonium sulphate is in equilibrium with an atmosphere which has relative humidity of 83·7%, but this value decreases slowly with increasing temperature to 80·0% at 30°C.[60] and to 79·1% at 37·8°C.[61] This variation has a direct bearing on the hygroscopicity of commercial ammonium sulphate; whereas the pure salt becomes hygroscopic at relative humidities above 80%, the commercial salt containing 0·10–1·50% of free sulphuric acid becomes hygroscopic at humidities above 68–70%, but after neutralization of the crystals by ammonia gas the commercial salt behaves exactly like the pure salt.[62] This indication that increased hygroscopicity is due to the presence of free sulphuric acid is supported by experiments in which sulphuric acid was added to pure ammonium sulphate.[63] It is also found that as little as 0·001% of pyridine sulphate on the crystal faces of ammonium sulphate may increase the hygroscopicity very considerably.[64] The property of caking during storage appears to be a function not only of the hygroscopicity, but also of the size and shape of the crystals in so far as these affect the percentage of voids in the bulk solid.[65] It is claimed that the crystalline form dissolves in water at twice the rate of the granular form, which does not cake on storage.[66]

ELECTRICAL PROPERTIES

The dielectric constant of solid ammonium sulphate measured in the powdered state has been determined as 7·92[69] and 8·20.[70] The dielectric constant of crystalline

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ammonium sulphate has been measured over the temperature range −100° to 0°C. and the curve showing variation with temperature has a discontinuity in the form of a very sharp peak at −53·4°C., as does the specific heat–temperature curve. Both the real and imaginary portions of the dielectric constant have similar curves.[71] This discontinuity is not believed to be due to spontaneous polarization.[72] Although the temperature at which the maximum occurs is independent of frequency, the dielectric constant at low temperatures decreases at wave-lengths of 10^5 cm. and increases rapidly in the centimetre range.[73] When the dielectric constant of a single crystal was measured at a frequency of 1440 kc. sec.^{-1} with the applied field parallel to the *a* axis, a sharp discontinuity was found at −36° on cooling and at −29°C. on warming. In the direction of the *b* or *c* axis much smaller discontinuities were found between −55° and −40°C., these taking the form of a change of slope, rather than a sharp peak.[74] Absorption of radiation of wave-lengths in the centimetre range was at a maximum at the same temperature at which the dielectric constant was maximal.[75]

Potential differences as high as 61 v. have been measured across the water–ice interface during the freezing of ammonium sulphate solutions. The actual potential is a function of the concentration of salt.[76] Potential differences have also been measured at the boundary of ammonium sulphate solutions and methanol, ethanol or acetone.[77] The use of ammonium sulphate in the Leclanché cell has been studied but the potential produced is less than that with ammonium chloride as electrolyte.[78]

REFRACTION AND OTHER OPTICAL EFFECTS

The refractive index and equivalent refractivity of solutions of ammonium sulphate at 25°C. both increase with concentration[42] as shown in Table VIII. The equivalent refractivity at infinite dilution is 11·70. Refractive indices have also been determined[43] at 25°C. for solutions of different concentrations from 0·489 to 7·830 normal.

Table VIII.—Refractive Index and Equivalent Refractivity of Solutions of Ammonium Sulphate

Molality	Refractive index n_D^{25}	Equivalent refractivity R_D
1·70760	1·34857	11·700
3·99962	1·36521	11·712
5·81062	1·37550	11·718
8·02032	1·38566	11·723
10·6389	1·39508	11·731

The equivalent refraction extrapolated to infinite wave-length is[79] 21·86 which is 1·78 units greater than the equivalent refraction of potassium sulphate. The difference is ascribed to the occurrence of hydrogen bonding between the hydrogen of the ammonium ion and the oxygen of the sulphate ion, each bond thus accounting for 0·21 units.[80] The following values have been obtained for the rotation of plane polarized light by crystals of ammonium sulphate in degrees per millimetre along the optical axis[81]: for light of wave-length 5790 A., 2·8°; for 5400 A., 3·05°; and for 4250 A., 4·0°.

The Rayleigh constant of light scattering by dilute solutions of ammonium sulphate[82] is 66×10^{-7}. The depolarization of light scattered by solutions has also been studied.[83] The frequencies in the Raman spectrum have been measured[84]; splitting of the degenerate lines was observed and related to deformation of the sulphate tetrahedron. The Faraday effect (rotation of the plane of polarization by a magnetic field) has been measured[43] at 0°C. with light of wave-length 5460 A. in solutions of 5·146 and 38·25 g./100 g., the respective Verdet constants being 0·0158 and 0·0167, and the corresponding molecular rotations, relative to water as unity, being 4·99 and 4·87. At 28°C. the magneto-optical rotation in the ultra-violet is independent of the concentration, but in the visible spectrum the molecular rotation increases with decreasing wave-length[85] or increasing concentration.[86]

Miscellaneous Properties

The magnetic susceptibility of anhydrous ammonium sulphate has been determined as 71·63[87] and 67·0 ± 0·70[88] $\times 10^{-6}$ e.s.u. The corresponding susceptibilities of the sulphate ion and the ammonium ion have been deduced as 37·55[87] and 42·9[89] $\times 10^{-6}$ e.s.u. No measurable paramagnetic absorption was found with static fields from 0 to 5000 œrsteds.[90] The velocity of sound has been determined in solutions of ammonium sulphate of various concentrations,[91] while the absorption of sound has been measured[92, 93] at frequencies up to 300 Mc. sec.$^{-1}$.

The adiabatic compressibility coefficient[67] determined from sound velocity measurements in an ammonium sulphate solution of mole fraction 0·004024 at 25°C. is $42{\cdot}469 \times 10^{-12}$.

The diffusion coefficient of ammonium sulphate in aqueous solution at 25°C. increases steadily from $0{\cdot}825 \times 10^{-5}$ at a concentration of 0·0525 molar to $1{\cdot}125 \times 10^{-5}$ at 3·594 molar.[68]

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PHASE RULE STUDIES INVOLVING AMMONIUM SULPHATE

There have been a number of phase rule studies involving ammonium sulphate as one of the components.

Anhydrous Systems

Studies of anhydrous systems have for the most part been confined to sulphates and nitrates. Complete solid solution has been verified between ammonium sulphate and potassium sulphate, but no solid solution occurs between ammonium sulphate and sodium sulphate at 70°C.[1] The system ammonium sulphate–ammonium nitrate yields mainly solid solutions[2] with two invariant points at 166° and 176°C., but the existence of two unstable compounds has been described, $(NH_4)_2SO_4,3NH_4NO_3$ and $(NH_4)_2SO_4,2NH_4NO_3$.[3] Ammonium nitrate and sodium sulphate form one pair of mixed crystals, NH_4NO_3–$(NH_4)_2SO_4$, and there is a ternary point at 118°C.[4] The reciprocal salt pair ammonium nitrate–potassium sulphate, however, forms three sets of mixed crystals, NH_4NO_3–KNO_3, $(NH_4)_2SO_4$–NH_4NO_3 and $(NH_4)_2SO_4$–KNO_3, which are in equilibrium at a ternary point at 156·5°C.[5]

Systems Containing Water

The simplest of the systems containing water consists of two branches, ice and ammonium sulphate, having a eutectic point at $-19{\cdot}0$°C., with 39·25% of ammonium sulphate and 60·75% of water. The ternary system ammonium sulphate–ammonia–water has been investigated from 5° to 35°C.[7] In the system ammonium sulphate–sulphuric acid–water at concentrations of sulphuric acid between 0 and 22% pure ammonium sulphate separates, between 22 and 55% the solid phase is the double salt $(NH_4)_2SO_4,NH_4HSO_4$, while above 55% ammonium hydrogen sulphate crystallizes.[8] Later work suggested that the following solid phases occur in the range 10–90°C.: $(NH_4)_2SO_4$; $4(NH_4)_2SO_4,H_2SO_4$; $3(NH_4)_2SO_4,H_2SO_4$; $(NH_4)_2SO_4,H_2SO_4$; $(NH_4)_2SO_4,3H_2SO_4$; and mixed crystals of $(NH_4)_2SO_4$ and $3(NH_4)_2SO_4,H_2SO_4$. The double salt $4(NH_4)_2SO_4,H_2SO_4$ appears to be stable only over the temperature range 30–50°C., while the mixed crystals were not obtained below 30°C. The salt $(NH_4)_2SO_4,H_2SO_4$ decomposes in aqueous solution below 30°C. At 98·3°C. the solid phases are stated to consist[12] of $(NH_4)_2SO_4$, $3(NH_4)_2SO_4,H_2SO_4$ and NH_4HSO_4 with intermediate regions of mixed crystals between successive compounds. The system ammonium sulphate–ammonium sulphite–water[6] has a ternary point at $-21{\cdot}5$°C. and concentrations of 30% ammonium sulphate and 10·5% ammonium sulphite. In the system ammonium sulphate–ammonium bisulphite–water[13] the solid phases are ammonium sulphate, ammonium metabisulphite and water, with no double salts or solid solutions, the ternary point being at $-34{\cdot}5$°C., with 50·5% of ammonium bisulphite and 10·0% of ammonium sulphate. The system ammonium sulphate–ammonium sulphite–ammonium bisulphite–water[14] has also been studied at 30°C. These systems containing sulphite and bisulphite are very important for the control of the sulphite–bisulphite process for the manufacture of ammonium sulphate.[15]

The system carbon dioxide–ammonia–ammonium sulphate–water has been thoroughly studied[16] by determining (*a*) the polytherms at 20°, 30°, 40° and 50°C. at atmospheric pressure for the system saturated with carbon dioxide and with ammonium bicarbonate and ammonium sulphate as solid phase; (*b*) the saturation concentrations of carbon dioxide and ammonia in the presence and absence of solid ammonium sulphate; and (*c*) the solubility polytherm of ammonium sulphate in the solution saturated with ammonia. The surfaces thus defined limit the space containing the equilibria of all compounds formed in saturated solution up to one atmosphere pressure. No double salts are formed with ammonium sulphate.

The Ammonia–Soda Process

The ammonia–soda process has been similarly studied[17–19] by determining the phase diagram of the reciprocal system sodium sulphate–ammonium bicarbonate–water. Solid phases identified by means of the polarizing microscope include ammonium sulphate and sodium ammonium sulphate. From the phase diagram empirical formulæ have been derived which enable the ionic concentrations to be calculated under various conditions. There are in this system three invariant points; one congruent, corresponding to the solid phases $(NH_4)_2SO_4 + Na_2SO_4$, $NaSO_4$,-$(NH_4)_2SO_4$,$4H_2O + NH_4HCO_3$ and two incongruent with solid phases Na_2SO_4,-$10H_2O + Na_2SO_4$, $(NH_4)_2SO_4$,$4H_2O + NH_4HCO_3$; and Na_2SO_4,$10H_2O + NaHCO_3 + NH_4HCO_3$.

Equilibrium in the system ammonium carbamate–ammonium sulphate–ammonia–water has been studied[20] in solutions saturated with ammonia and from 20° to 80°C. The presence of ammonium sulphate has little effect on the solubility of either ammonia or ammonium carbamate. The system ammonium sulphamate–ammonium sulphate–water has three invariant points.[21]

Systems Containing Chlorides

No double salts or mixed crystals are formed with ammonium chloride,[22] but with potassium chloride mixed crystals are formed in all ratios between potassium sulphate and ammonium sulphate.[23] The system ammonium sulphate–sodium chloride–water has been studied at temperatures from 0° to 80°C. This system[24] may be represented by a pyramidal model which at 80°C. is divided into twelve regions, one region of unsaturated solution only, four regions of single salts and a solution, five regions of pairs of salts (forming solid solutions) and a solution and two regions with three salts and a solution. There is an invariant point at 50°C. where the solid phase is anhydrous sodium sulphate, ammonium sulphate, the double salt, Na_2SO_4,-$(NH_4)_2SO_44H_2O$, and ammonium chloride. At 40°C., owing to the stability of sodium sulphate decahydrate, the diagram is divisible into sixteen regions with an invariant point at 26·5°C. The composition of the solid phases and mother liquors, and the formation of solid solutions has been examined in the systems ammonium sulphate–potassium chromate–water and ammonium sulphate–potassium chloride–water.[25]

Systems Containing Nitrates, etc.

In the system ammonium sulphate–ammonium nitrate–water it has been claimed that the only double salt formed[26] is $(NH_4)_2SO_4$,$2NH_4NO_3$, melting at 310°C., but polythermal analysis disclosed the existence in addition of the salts:$(NH_4)_2SO_4$,-$3NH_4NO_3$ and $(NH_4)_2SO_4$,$4NH_4NO_3$; crystal data for the first of these are given.[27] In the system ammonium sulphate–potassium nitrate–water a series of solid solutions of salts is formed from all possible combinations of the ions and in addition the double salt $2(NH_4)_2SO_4$,$3NH_4NO_3$ is reported.[28] In this system a new series of solid solutions has been found consisting of the salt $(NH_4)_2SO_4,2NH_4NO_3$ and a metastable double salt $K_2SO_4,2KNO_3$.[29] In the system ammonium sulphate–orthophosphoric acid–water the solid phases consist of ammonium sulphate and a double salt $(NH_4)_2H_3SO_4PO_4$ at 25° and 70°C.[30] No double salts are found in aqueous solutions of ammonium sulphate and ammonium dihydrogen phosphate,[31] diammonium hydrogen phosphate,[32] or ammonium molybdate.[33] The system ammonium sulphate–ammonium chromate–water forms a series of mixed crystals, the diagram being of the Roozeboom type V,[34, 35] but two complete series of solid solutions are formed between ammonium sulphate and potassium chromate.[36] Ternary and quaternary equilibria have been studied at 25° and 60°C. for the reciprocal salt pair ammonium sulphate–sodium perchlorate,[37] while the systems including ammonium and sodium borate have been investigated in great detail.[38, 39]

Systems Containing Sulphates

Since ammonium sulphate readily forms double salts and alums there have been many investigations of systems including other metallic sulphates. It is convenient to consider these by Periodic groups. In the first group lithium sulphate forms a double salt $Li_2SO_4,(NH_4)_2SO_4$ and the solubility isotherms show two ternary eutectics, one composed of lithium sulphate monohydrate, double salt and ice at -30°C., the other composed of ammonium sulphate, double salt and ice at -27°C. The heat of formation of the double salt[40] is $1{\cdot}28 \pm 0{\cdot}01$ kcal. At 0° and 25°C. discontinuous solid solutions are formed between lithium sulphate monohydrate and the double salt.[41] Equilibrium in the quaternary system ammonium sulphate–lithium sulphate–water–sulphuric acid has also been studied.[42] The double salt $Na_2SO_4,(NH_4)_2SO_4,4H_2O$ has been found to occur as a solid phase in aqueous systems of ammonium sulphate with sodium sulphate[43] or sodium and potassium sulphates.[44] This double salt is decomposed by high concentrations of ammonia.[45] The solubility diagram of the system ammonium sulphate–potassium sulphate–water has only two areas, ice and continuous solid solutions of the two salts.[46] The curve connecting the two eutectic branches, at $-1{\cdot}55$°C. and 18·85°C., has no maximum and is only slightly convex, indicating complete isomorphism between the two salts.[47] At 30°C. potassium sulphate alone is the solid phase for concentrations of ammonium sulphate from 0 to 58·6%, while ammonium sulphate alone crystallizes at concentrations greater than 71·92%, the gap being bridged by mixed crystals.[48] Continuous solid solutions are also formed in systems including cæsium sulphate or rubidium sulphate, the former belonging to Roozeboom type II, the latter to Roozeboom type I.[49]

The following double salts are formed with group II metals:

$BeSO_4,(NH_4)_2SO_4,2H_2O$ and $BeSO_4,(NH_4)_2SO_4$,[50–52]
$MgSO_4,(NH_4)_2SO_4,6H_2O$,[53–56] $CaSO_4,(NH_4)_2SO_4,H_2O$,
$2CaSO_4,(NH_4)_2SO_4$, $5CaSO_4,(NH_4)_2SO_4,H_2O$,[57]
$ZnSO_4,(NH_4)_2SO_4,6H_2O$,[58–62] $CdSO_4,(NH_4)_2SO_4,6H_2O$,[63, 64]
$[Cd(NH_3)_4(H_2O)_2]SO_4,(NH_4)_2SO_4$, $[Cd(NH_3)_5(H_2O)]SO_4,(NH_4)_2SO_4$.[64]

When solid solutions are formed between double salts containing zinc, copper or nickel, the relation between molar concentration in solution and in solid phases can be expressed by an exponential equation.[60] The microstructure and refractive index of the zinc double salt have been determined.[61]

The system ammonium sulphate–aluminium sulphate–water has been studied[65–67] at various temperatures from 0° to 40°C. A continuous series of solid solutions is formed between ammonium and potassium alums and also between ammonium aluminium alum and ammonium iron alum, but no solid solutions are formed between ammonium and sodium alums.[67] The system cerous sulphate–ammonium sulphate–water has been studied from 0° to 99·5°C.,[68–71] the double salts $Ce_2(SO_4)_3,(NH_4)_2SO_4,8H_2O$ and $Ce_2(SO_4)_3,5(NH_4)_2SO_4$ being identified and described crystographically.[70] The double sulphates formed with the rare earth metals generally are of the types:

$$X_2^{\cdots}(SO_4)_3,(NH_4)_2SO_4,2 \text{ or } 8H_2O, \quad X_2^{\cdots}(SO_4)_3,5(NH_4)_2SO_4$$
$$2X_2^{\cdots}(SO_4)_3,5(NH_4)_2SO_4 \text{ and } X_2^{\cdots}(SO_4)_3,2(NH_4)_2SO_4,9H_2O$$

although other types may occur.[70] Complete crystallographic data have been obtained for the neodymium double salt, $Nd_2(SO_4)_3,(NH_4)_2SO_4,8H_2O$.[71] Thallous sulphate forms no double salts but a continuous series of solid solutions with ammonium sulphate.[72]

Thorium, the only representative of group IV, forms the double salts[73]: $Th(SO_4)_2,3(NH_4)_2SO_4,3H_2O$, $Th(SO_4)_2,2(NH_4)_2SO_4,3{\cdot}5H_2O$ and $Th(SO_4)_2,(NH_4)_2SO_4,5H_2O$. Bismuth, in group V, forms $Bi_2(SO_4)_3,3(NH_4)_2SO_4$. The solubility curve of the system with uranyl sulphate at 25°C. shows the existence of[75, 76] $2UO_2SO_4,(NH_4)_2SO_4,5H_2O$ and $UO_2SO_4,(NH_4)_2SO_4,2H_2O$. Manganese in group VII forms the salt: $MnSO_4,(NH_4)_2SO_4,6H_2O$,[77, 78] but conductivity measurements of the system at 15°, 25° and 35°[79] indicate that there must exist in addition in solution complexes of the type $MnSO_4,n(NH_4)_2SO_4$, where n depends on the salt concentration in solution. If ammonium sulphate is added to solutions of $Fe_2(SO_4)_3,6H_2O$ or $Fe_2(SO_4)_3,H_2SO_4,2H_2O$ the composition of the liquid phase remains practically constant with increasing concentration of ammonium sulphate, while the solid phase is converted from the hydrated acid ferric sulphate into anhydrous ferric ammonium alum $Fe_2(SO_4)_3,(NH_4)_2SO_4$, no solid solutions being formed. If, however, the solution is $Fe_2(SO_4)_3,H_2SO_4,8H_2O$ in equilibrium with the solid phase $Fe_2(SO_4)_3,H_2SO_4$, a continuous series of solid solutions is formed with ammonium sulphate.[80] Addition of sulphuric acid to a solution at 100°C. in equilibrium with $Fe_2(SO_4)_3(NH_4)_2SO_4$ converts this salt back to the acid ferric sulphate. The interconversion is attributed to replacement of the ammonium ion by the oxonium ion, as may be seen by writing the formulæ in the complex form:

$$[NH_4]^+[Fe(SO_4)_2]^- + H_3O^+ \rightleftharpoons [H_3O]^+[Fe(SO_4)_2]^- + NH_4{}^+$$

The similarity between these two compounds is shown by crystallographic examination and by the fact that they form continuous solid solutions. If iron ammonium alum, $Fe_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$, is heated to 170°C. with sulphuric acid, a basic salt is formed which is claimed to have the formula[81]

$$[(OH)_2{\cdot}Fe{\cdot}SO_4{\cdot}Fe(OH)_2{\cdot}SO_4{\cdot}Fe(OH)_2]^- \ (NH_4)^+$$

Copper forms the double salt $CuSO_4,(NH_4)_2SO_4,6H_2O$, stable over a very wide range of concentration and between $Cu{:}2NH_4$ ratios of 3:1 and 1:137.[82] Solid solutions and double salts are formed in the system copper sulphate–ammonium sulphate–potassium sulphate–water.[53] Addition of nickel or cobalt sulphate to a solution of ammonium sulphate causes immediate separation of the double salt with no increase in the solubility of ammonium sulphate.[62] Silver sulphate forms no solid solutions or double salts with ammonium sulphate.[83]

Miscellaneous Systems

The distribution coefficients of various anions have been determined between the water and alcohol layers in the system water–ethanol–ammonium sulphate,[84] while the system water–ammonium sulphate–propanol has been studied from the point of salting-out of the alcohol.[85] Phase equilibrium studies have been carried out with the systems: ammonium sulphate–sulphuric acid–ethanol,[86] ammonium sulphate–water–*tert*.-butanol,[87] ammonium sulphate–water–*cyclo*hexanone oxime,[88] ammonium sulphate–water–pyridine[89] and ammonium sulphate–water–ϵ-caprolactam.[90]

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CHEMICAL REACTIONS

Action of Heat on Ammonium Sulphate

When ammonium sulphate is strongly heated it decomposes, losing ammonia and water to form ammonium hydrogen sulphate, the compound NH_4HSO_4,H_2SO_4 and finally ammonium pyrosulphate.[1] Sulphamic acid may also be formed and the sulphur dioxide and nitrogen which have been detected escaping from strongly heated ammonium sulphate probably arise from the decomposition of this sulphamic acid. When ammonium sulphate is heated to 400°C. for an hour the residue consists of ammonium sulphate 10%, ammonium hydrogen sulphate 14%, ammonium

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pyrosulphate 70% and sulphamic acid 6%.[2] Ammonium hydrogen sulphate may be prepared by heating ammonium sulphate above the melting point in a silica vessel so that ammonia may escape freely.[3] This decomposition:

$$(NH_4)_2SO_4(s) \rightarrow NH_4HSO_4(s) + NH_3(g)$$

has a heat change $\Delta H_{298\cdot16}$ of 25,940 g.-cal. per mol. and an entropy change $\Delta S_{298\cdot16}$ of 25·93 g.-cal. per deg.[4] The derived heat and free energy of reaction are,[4] in kcal./mol.$^{-1}$,

$$\begin{aligned}\Delta H &= 27{,}200 - 7{\cdot}65T + 9{\cdot}95\times10^{-3}T^2 + 0{\cdot}398\times10^5T^{-1}\\ \Delta F &= 27{,}200 + 17{\cdot}61\,T\log T - 9{\cdot}95\times10^{-3}T^2 + 0{\cdot}199\times10^5T^{-1} - 71{\cdot}00T\end{aligned}$$

Corresponding equations are given for the decomposition to liquid ammonium hydrogen sulphate, and data are available for calculating ΔH and ΔF at any temperature from 298·16°K. to 1000°K. The formation of ammonia is slight at the melting point of ammonium hydrogen sulphate, and an equilibrium pressure of ammonia of one atmosphere does not occur until a temperature of 873°K. is reached.[4]

For the overall decomposition[4]:

$$(NH_4)_2SO_4(s) \rightarrow 2NH_3(g) + H_2O(g) + SO_3(g)$$

$$\begin{aligned}\Delta C_p &= 10{\cdot}48 - 46{\cdot}3\times10^{-3}T - 3{\cdot}919\times10^5T^{-2}\\ \Delta H &= 104{,}920 + 10{\cdot}48T - 23{\cdot}15\times10^{-3}T^2 + 3{\cdot}919\times10^5T^{-1}\\ \Delta F &= 104{,}920 - 2{\cdot}414\,T\log T + 23{\cdot}15\times10^{-3}T^2 + 1{\cdot}959\times10^5T^{-1} - 87{\cdot}18T\\ \Delta H_{298\cdot16} &= 107{,}300 \text{ g.-cal. mol.}^{-1}\\ \Delta S_{298\cdot16} &= 145{\cdot}79 \text{ g.-cal. deg.}^{-1}\end{aligned}$$

A phase diagram has been prepared for the system sulphuric acid–ammonia.[1] This shows that, in addition to the neutral salt and the hydrogen sulphate, the compounds $(NH_4)_2SO_4,H_2SO_4$ and $(NH_4)_2SO_4,3NH_3$ exist. From anhydrous solutions of ammonium sulphate in sulphuric acid there have been isolated the two compounds[5]: $(NH_4)_2SO_4,3H_2SO_4$, m.p. 48·0°C.; and $(NH_4)_2SO_4,H_2SO_4$, m.p. 146·9°C. The double salt $(NH_4)_2SO_4,HSO_3NH_2$ is obtained on cooling an aqueous solution[1] of ammonium sulphate and sulphamic acid.[6]

The reaction of ammonia and sulphur trioxide gives a mixture of complex products, among which have been identified diammonium imidosulphate, ammonium imidosulphate dihydrate, ammonium amidosulphate and ammonium sulphate.[7] The actual products depend on the ratio of ammonia to sulphur trioxide. At about unit molar ratio ammonium sulphamate and ammonium sulphate are the chief products.[8] Between 5 and 14% of ammonium sulphate is formed by the reaction of ammonia and solid sulphur trioxide at −38°C. or −76°C.[9] A method of analysing the mixture of compounds has been developed,[10] and crystallographic data and optical properties are available for some of the products.[7] The solubility of ammonium imidosulphate in both water and aqueous ammonia has been determined between 0° and 60°C.[11] Sulphur dioxide and ammonia react near 0°C. to form ammonium amidosulphinate or the corresponding acid. At higher temperatures the condensation products decompose to form a mixture of amido compounds, ammonium sulphate, ammonium hydrogen sulphate, amidosulphinic acid and other compounds.[12] The hydrolysis of amidosulphinic acid, NH_2SO_2H, yields ammonium hydrogen sulphite, ammonium sulphate and ammonium trithionate.[13]

The decomposition temperature at which gas is first evolved has been determined for mixtures of ammonium sulphate and potassium sulphate. From a temperature of 248°C. for pure ammonium sulphate, the decomposition temperature falls to a minimum of about 240°C. at 42 mol.-% of ammonium sulphate and then rises again as the mole percentage decreases.[14]

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Equilibria with HCl, $NaHCO_3$ and D_2O

Equilibrium in the system:

$$(NH_4)_2SO_4 + 2HCl \rightleftharpoons H_2SO_4 + 2NH_4Cl$$

has been studied by analysing solid and liquid phases after equilibrium had been attained at 25°C. In addition to the normal and acid sulphates, the double salt $(NH_4)_2SO_4,NH_4HSO_4$ was found, but the salt NH_4HSO_4,H_2SO_4 was not formed. Congruent points were found only in the region of three component systems and not among the invariant points of four component systems.[15]

The equilibrium of the system:

$$Na_2SO_4 + 2NH_4HCO_3 \rightleftharpoons 2NaHCO_3 + (NH_4)_2SO_4$$

has been studied at various temperatures and under different pressures of carbon dioxide.[16] Determinations have also been made of the equilibria of two-, three- and four–component systems made up from the four salts.[17] The double decomposition between sodium formate and ammonium sulphate has been investigated at 13·5°, 24·6° and 60°C.[18] The kinetics of exchange of hydrogen and deuterium have been studied between ammonium sulphate and deuterium oxide in the presence and absence of an excess of free sulphuric acid.[19] Exchange is very slow with the hydrogen of the ammonium ion but practically instantaneous with that of ammonia. The kinetics can be represented by the equation:

$$-\ln(1-\alpha) = 2kW[1 + (N/(W+B))]t$$

where α is the rate of exchange, W, N and B are the concentrations respectively of water, salt and free acid, and k is the rate constant of the hydrolysis of the ammonium ion. Although in strongly acid solutions the concentration of free ammonia is decreased by a factor of 10^5, the rate of exchange is decreased only by a factor of 10.

Reactions with Oxidizers

The reaction of bromine with aqueous solutions of ammonium sulphate, alone and mixed with manganous sulphate, has been studied at different degrees of acidity and with various concentrations of alkali acetate.[20] Each of the reactions is progressively retarded by increased acid concentration and progressively accelerated by an increased acetate concentration. In neutral solution the reaction: $2NH_4^+ + 3Br_2 = 6Br^- + N_2 + 8H^+$ is quantitative, but slightly more than the theoretical quantity of bromine is used, a fact which is explained by assuming that oxidation occurs through the intermediate formation of hypobromous acid.

In the presence of potassium permanganate and hydrogen peroxide, ammonium sulphate hydrolyses to liberate sulphuric acid which reacts with the manganic oxide present, thus disturbing the equilibrium and causing further hydrolysis until the ammonium sulphate is completely decomposed according to the reaction[21]:

$$K_2Mn_2O_8 + 5H_2O_2 + 3(NH_4)_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2 + 6NH_3$$

Fluorine reacts with an aqueous solution of ammonium sulphate liberating ozonized oxygen and forming ammonium persulphate.[22] In a study of heterogeneous reactions in a silent electric discharge, hydrogen was found to reduce solid ammonium sulphate to hydrogen sulphide and ammonia under an applied potential of 15,000 v.[23] The oxidation of ammonium sulphite to sulphate by air or oxygen was not accelerated by supersonic radiation but was occasionally retarded.[24]

Electrolysis and Conversion Into Ammonium Persulphate and Nitrate

When a solution of ammonium sulphate is electrolysed with a mercury cathode at room temperature ammonium amalgam is formed above pH 4. The formation of amalgam is suppressed by raising the temperature to about 50°C. or by adding impurities such as ammonium sulphide.[25] Ammonium persulphate may be prepared by the electrolysis of a solution of ammonium sulphate using a platinum or lead anode.[26, 27] By electrolysis of a 2·5 N. solution of ammonium sulphate 0·0045 mole of persulphate is produced per ampere-hour, which is the highest yield obtained from any metal sulphate.[28] At high concentrations the anode current efficiency increases with current density to a maximum of about 80% but the opposite effect is observed at low concentrations.[29] The yield is increased by the presence in solution of potassium ion or fluoride ion (0·2%),[28] the effect increasing with concentration up to a maximum and then decreasing. It has been suggested that this catalytic effect is due to the action of the electric fields of the ions on the electron rearrangements occurring at the anode.[30] High yields of persulphate have also been reported after the addition of 0·5% of ceric sulphate, 0·1% of sodium chromate and 0·1% of ferric chloride,[31] but magnesium, cadmium, manganese, cobalt, aluminium and zinc ions are said to decrease the yield.[28] Electrolysis of a saturated solution of ammonium sulphate 4 N. in sulphuric acid results in the continuous production of solid ammonium persulphate, of 80–85% purity,[32] the acid altering the solubility relations in such a way that the ammonium sulphate is in equilibrium with a lower concentration of persulphate which thus separates out.

Considerable amounts of ammonia are oxidized to nitrate and other compounds when solutions of ammonium sulphate are exposed to light.[33]

Action on Polymers and Organic Compounds

There have been a number of investigations into the effects of ammonium sulphate on the properties of polymers and colloid systems. Thus the formation of silica gels from sodium silicate solutions containing ammonium sulphate may involve the formation of a readily coagulated ammonium salt of silicic acid of intermediate molecular weight.[37] The heating of fibres of regenerated cellulose and of polyvinyl alcohol in solutions of ammonium sulphate has been shown to result in some degree of depolymerization.[38, 39] The 'flocculation point' (salt concentration at which precipitation occurs) has been determined for ammonium sulphate with various cellulose ethers.[40] Ammonium sulphate solutions have been used to titrate cellulose peptized in cuprammonium solutions. The solvent action of the cuprammonium decreases as sulphate ion concentration increases until the cellulose suddenly separates.[41] Whereas silica gel does not selectively adsorb cations from ammonium sulphate solution, alumina gel shows both anion and cation adsorption, and a mixed silica–alumina gel behaves like a strong acid exchanger adsorbing only ammonium ions from solutions.[42]

Precipitates of barium sulphate prepared by adding barium salicylate to ammonium sulphate are actually solid solutions of barium sulphate and ammonium sulphate. From the results of *X*-ray examination it is concluded that the contaminant is not arranged in the lattice in an orderly manner.[34] Ammonium sulphate is an effective catalyst for the dehydration of castor oil by heating to 240°C.[35]

The interphase in the system ammonium sulphate–ethanol–water consists of molecules of ethanol, so that the separation of phases is a salting out of ethanol. The significance of this for the separation of colloidal solutions is discussed.[43] The interaction between collagen and ammonium sulphate solution has been studied by measuring the membrane potential of the collagen.[44] Ammonium sulphate at N. concentration causes only a slight spreading of the interfibril spacing in collagen.[45] Monolayers of collagen stable over the whole pressure range have been produced on a 30% solution of ammonium sulphate.[46] Monolayers of di- and polyphenols,[47] styrene–vinylpyridine copolymers[48, 49] and α-aminolauric acid polymers[50] have been prepared on solutions of ammonium sulphate. Substances with low dielectric constants have been found to hinder the coagulating action of ammonium sulphate solutions on colloids such as casein and albumin.[51] Studies have also been carried out on the effect of ammonium sulphate on the turbidity of protein solutions[52] and on the stability of emulsions.[53–55]

Miscellaneous Effects

A large number of double salts formed by ammonium sulphate and other metal sulphates has already been discussed (see page 491), but a few additional salts are dealt with below. The homology of the fluoroberyllate and sulphate ion is confirmed by thermometric and conductimetric titrations of the ammonium salts with sulphuric acid which show that similar double salts are formed with the acid.[56] Double salts are formed with ammonium dihydrogen phosphate, $(NH_4)_2SO_4,NH_4H_2PO_4$,[57] with zirconium sulphate, $(NH_4)_2H_2ZrO(SO_4)_3$,[58, 59] and with uranyl sulphate, the last being an insoluble compound analysing as $3NH_3{\cdot}4UO_3{\cdot}2SO_3,xH_2O$.[60] Spectrophotometric studies of solutions containing copper sulphate and ammonium sulphate indicate that complex ions are formed with two and with four molecules of ammonia per copper atom,[61] but potentiometric titration discloses in addition a six to one complex.[62] Viscosity studies at 20°C. of mixtures of ammonium sulphate and zinc sulphate indicate that only one complex,[63] $(NH_4)_2SO_4,2ZnSO_4$, is formed, but interfacial tension measurements indicate that ammonium sulphate forms two complexes in solution with zinc, copper, nickel, cobalt, magnesium and cadmium sulphates.[64]

Ammonium sulphate has been found to occur in the hygroscopic nuclei ($> 10^{-12}$ g.) present in air[65] and is also responsible for the 'bloom' or 'blue fogging' of varnish and enamel coatings.[66, 67] The deterioration of jute bags treated with cuprammonium solutions has been found to be due to sulphuric acid produced by hydrolysis of traces of ammonium sulphate.[68, 69] The destructive action of ammonium sulphate solutions on concrete and cement is due to reaction of the calcium ions with the sulphate ions.[70, 71] Ammonium sulphate increases the rate of water absorption and setting of plaster of Paris but decreases the mechanical strength.[72]

The freezing point constant of paraldehyde in solutions of ammonium sulphate increases with dilution indicating that polymerization is occurring.[73] Studies have been made of the course of extraction of ammonium sulphate adsorbed on kaolin, bone black and blood charcoal and the results are shown to be accurately described by an equation derived from the Freundlich isotherm.[74, 75]

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APPLICATIONS

As Fertilizer

In spite of doubts that have been expressed from time to time, ammonium sulphate retains its position as the most widely used synthetic nitrogen fertilizer.[1, 2] Although other ammonium salts and urea are as effective fertilizers as ammonium sulphate, they are inferior as regards cost or hygroscopicity.[3, 4] Ammonium sulphate is leached from the surface layers of soil slightly faster than is sodium nitrate, an effect which appears to be due to increased soil permeability.[5] It is stated to increase soil acidity significantly only in the immediate locality of the point of application and also to increase the availability of phosphate from ground phosphate rock applied in admixture.[6] A number of processes have been developed for producing mixed fertilizers by treating ammonium sulphate with phosphoric acid or minerals containing calcium phosphate so as to produce a mixture of ammonium sulphate and ammonium phosphates.[7–12] At high rates of application ammonium sulphate is an effective herbicide for the control of weeds,[13] while in conjunction with ferrous sulphate,[14] with or without the addition of selective weed killers[15] or with zinc sulphate,[16] effective control of mosses is obtained.

As Fire-retardant

Ammonium sulphate is used as a fire retardant, either alone[17] or compounded with other substances[18, 19] such as synthetic resins or wetting agents, for treating timber and for flame-proofing cellulose fabrics.[20] Addition of 0·1–1·0% to cigarette paper is said to improve the ashing properties,[21] while a sludge of aqueous ammonium sulphate, bentonite and waste fibre has been suggested as a composition for extinguishing fires.[22]

In Glass-making

Addition of ammonium sulphate in amounts up to 1% of the batch in glass making is found to accelerate both the melting and refining processes.[23, 24] Most of the ammonia escapes during melting and reaction occurs with the sodium and calcium carbonates to form sulphates.[25, 26] When glass is heated to about 570°C. with ammonium sulphate, ammonium ion exchanges with sodium ion to produce a surface from which very much less alkali is leached by water superheated to 125°C.[27]

Miscellaneous Applications

A small percentage of ammonium sulphate mixed with ammonium nitrate reduces the hygroscopicity of the latter and stabilizes it against the physical disintegration caused by temperature variations,[28, 29] without affecting its explosive properties.[30, 31]

Addition of 4 to 6% of ammonium sulphate to the dye vat improves the 'levelling' properties of dyes on wool and semi-wool materials, acetate rayon and plant fibres[32–35]; for this purpose the salt is regarded as superior to ammonium acetate or sodium sulphate.

Aluminium salts have been extracted from clay by heating with ammonium sulphate for about 26 hr. at 430–450°C. to give a yield of aluminium oxide of over 97% of the theoretical.[36] Aluminium sulphate, produced by treating silicate ores

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with sulphuric acid, has been purified through the ammonium alum.[37, 38] A similar process has been applied to bauxite ores.[39] Ammonium sulphate is a useful flux for treating ilmenite (ferrous titanate)[40] and is added to the electrolyte bath in the refining or plating of iron,[41] manganese[42] and chromium.[43] The salt is also used in pickling baths for ferrous metals.[44]

Ammonium thiosulphate is prepared by mixing hot, concentrated solutions of sodium thiosulphate and ammonium sulphate, the resulting sodium sulphate being first separated by cooling.[45] Hydrogen peroxide may be produced by electrolysing a solution containing ammonium sulphate and sulphuric acid to form ammonium persulphate; the solution is then distilled in vacuo.[46] Ammonium sulphate is the most important agent for hydration of anhydrite to gypsum.[47] Melamine is prepared by heating a mixture of hydrogen cyanide, ammonia and ammonium sulphate.[48]

Ammonium sulphate solutions have been used as a coagulating bath in the preparation of viscose fibres.[49] The nitrogen content of steel has been increased to 0·01% by the addition of ammonium sulphate and calcium cyanamide to the ladle with consequent improvement of the machining properties.[50] Electrolytic etching by aqueous ammonium sulphate applied to samples with welds may be used to develop the austenite grain structure in the weld decay zone.[51] A paste containing potassium permanganate and ammonium sulphate is stated to be effective for descaling large iron structures.[52] The cold stability of beer may be assessed by titrating with a saturated solution of ammonium sulphate until a turbidity is just produced.[53] Ammonium sulphate and zinc oxide have been found to increase the speed of coagulation of rubber latex.[54] The salt has also been found useful in water purification.[55] The addition of small amounts of ammonium sulphate has been found to improve greatly the efficiency of many fermentation processes, such as the production of *d*-lactic acid from Jerusalem artichokes,[56] of ethanol from sweet potato,[57] molasses,[58] cane juice[59] and Chinese native sugar[60] and of aureomycin and vitamin B_{12},[61] but it is not advantageous in the production of butanol from cane sugar.[62]

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ANALYSIS

Paper chromatography has not proved very useful for the separation of ammonium sulphate from other salts,[1] while a careful study showed that alumina was not suitable for column chromatography owing to preferential adsorption of the cation.[2] A high-frequency conductivity method has been adapted to continuous measurement of the concentration of flowing solutions of ammonium sulphate over the concentration range 0–14% with an accuracy of 2·6%.[3] The acidity of ammonium sulphate measured by an electrometric titration gave results 0·01–0·02% lower than the standard methyl orange titration. An electrometrically neutral solution of the commercial salt was slightly acid to methyl orange because of the presence of traces of pyridine sulphate.[4] A method based on the liberation of iodine from a mixture of potassium iodide and potassium iodate also gave results for acidity lower than the methyl orange method.[5] The degree and uniformity of impregnation of pine wood by ammonium sulphate could be determined by an *X*-ray method with an accuracy

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greater than that given by the chemical method which required seven to ten times as long to carry out.[6]

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AMMONIUM HYDROGEN SULPHATE

Physical Properties

The melting point of ammonium hydrogen sulphate has been found to be 146·9° ± 0·5°C.[1] and 417°K. (143·9°C.).[2, 3] The heat of fusion is 3420 g.-cal. mol.$^{-1}$ and the entropy of fusion[2] 8·20 g.-cal. mol.$^{-1}$ deg.$^{-1}$ The heat content in excess of the value at 298°C. has been determined for temperatures from 350° to 600°K. and ranges from 1880 g.-cal. mol.$^{-1}$ at 350°K. to 17,940 g.-cal. mol.$^{-1}$ at 600°K. The following equations can be used to calculate the heat content at any temperature within this range[3]: for the solid from 98–417°K.

$$H_T - H_{298} = 10{\cdot}00 + 0{\cdot}0405T^2 - 6{\cdot}582$$

for the liquid from 417–600°K.,

$$H_T - H_{298} = 16{\cdot}06 - 0{\cdot}0374T^2 - 5160$$

For the reaction[2]:

$$(NH_4)_2SO_4 \rightarrow NH_4HSO_4(s) + NH_3(g)$$

ΔH_{298} is 25,940 g.-cal. mol.$^{-1}$ and ΔS_{298} is 25·93 g.-cal. deg.$^{-1}$ Data are available for the heat and free energy of reaction at temperatures from[2] 298·16°K. to 1000°K. The following heats and entropy changes[2] apply to the reaction:

$$NH_4HSO_4(s) \rightarrow NH_3(g) + H_2O(g) + SO_3(g)$$

$$\begin{aligned}
\Delta H_{298{\cdot}16} &= 81{,}360, \quad \Delta S_{298{\cdot}16} = 119{\cdot}86 \\
\Delta C_p &= 18{\cdot}13 - 66{\cdot}2 \times 10^{-3}\,T - 3{\cdot}521 \times 10^5\,T^{-2} \\
\Delta H &= 77{,}720 + 18{\cdot}13T - 33{\cdot}1 \times 10^{-3}\,T^2 + 3{\cdot}521 \times 10^5\,T^{-1} \\
\Delta F &= 77{,}720 - 41{\cdot}75\,T \log T + 33{\cdot}1 \times 10^{-3}\,T^2 + 1{\cdot}760 \times 10^5\,T^{-1} - 16{\cdot}18T
\end{aligned}$$

At the melting point $\Delta H_{417} = 81{,}360$ g.-cal. mol.$^{-1}$ and $\Delta S_{417} = 117{\cdot}10$ g.-cal. deg.$^{-1}$ for the solid salt and $\Delta H_{417} = 76{,}950$ g.-cal. mol.$^{-1}$ and $\Delta S_{417} = 108{\cdot}90$ g.-cal. deg.$^{-1}$ for the liquid. The extent of this reaction is negligible at the melting point of ammonium hydrogen sulphate, an equilibrium pressure of one atmosphere requiring a temperature of 678°K. This may be merely a question of reaction rates, although the solubility of ammonium sulphate in the hydrogen sulphate may be a factor. The specific heat in g.-cal. g.$^{-1}$ of ammonium hydrogen sulphate is given by[3]:

$$\begin{aligned}
&C_p = 10{\cdot}00 + 81{\cdot}0 \times 10^{-3}T \quad \text{for the solid} \\
\text{and} \quad &C_p = 16{\cdot}06 + 74{\cdot}8 \times 10^{-3}T \quad \text{for the liquid}
\end{aligned}$$

The density and viscosity of aqueous solutions of ammonium hydrogen sulphate have been determined[4] at 0°, 10°, 25°, 40° and 60°C.; the values at 25°C. are given in Table IX.

Table IX.—Density and Viscosity of Aqueous Solutions of Ammonium Hydrogen Sulphate at 25°C.

Molality	Density, d_4	Viscosity, *cp.*
0·5	1·0232	1·2250
1·0	1·0433	1·2850
3·0	1·0488	1·4300
5·0	1·1542	1·5500

The inner friction relative to water of solutions of ammonium hydrogen sulphate has been determined at 20°, 40°, 60° and 80°C. at various concentrations.[5] The relative inner friction of solutions of molarity 0·4375, 0·875, 1·75 and 3·5 is respectively 0·01089, 0·01196, 0·01455 and 0·02394, agreeing exactly with the values obtained with equimolar solutions of ammonium sulphate and sulphuric acid. The density, viscosity and apparent molar volume have been determined for solutions of ammonium hydrogen sulphate ranging from 0·0964 to 1·300 molar in anhydrous sulphuric acid.[6]. The surface tension of aqueous solutions of ammonium sulphate at 20°C. is given[7] in Table X.

Table X.—Surface Tension of Aqueous Solutions of Ammonium Hydrogen Sulphate, at 20°C.

Concentration (molar)	3·500	1·750	0·875	0·4375
Surface tension, dynes per cm.	77·92	74·91	73·96	73·11

The specific conductivity of molten ammonium hydrogen sulphate ranges[8] from 0·067 ohm^{-1} cm.$^{-1}$ at 136°C. to 0·143 ohm^{-1} cm.$^{-1}$ at 191·5°C. The conductivity of the melt follows the exponential relation:

$$\sigma = Ae^{-E_\sigma/RT}$$

where E_σ, the activation energy, is 5·3 kg.-cal. mol.$^{-1}$ and the constant A is 43. The specific conductivity and molar conductivity have also been determined in sulphuric acid from 0·1 to 1·0 molar.[6] Raman spectra[9] have been recorded for ammonium hydrogen sulphate and for the double salt $(NH_4)_2SO_4,NH_4HSO_4$.

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Chemical Properties

Although ethanol has no action on ammonium sulphate, it removes sulphuric acid from ammonium hydrogen sulphate to form the salt $(NH_4)_3H(SO_4)_2$, which is not deliquescent and melts with decomposition. Commercial ammonium hydrogen sulphate is stated to contain a certain amount of this acid salt.[1] When this triammonium hydrogen disulphate is treated with more anhydrous ethanol there is a slight fall in acidity, which is explicable if the hydrogen sulphate is regarded as a compound of the neutral salt and sulphuric acid from which the ethanol removes acid to form a ternary system.[2] The action of ethanol on ammonium hydrogen sulphate is claimed to yield a product containing 60–70% of the normal salt, and extraction of the anhydrous hydrogen sulphate in a Soxhlet apparatus to remove sulphuric acid leaving the normal sulphate.[3] Ammonium hydrogen sulphate and ammonium nitrate form a double salt, NH_4HSO_4,NH_4NO_3, melting at 87°C., soluble in water and very hygroscopic. The solubility of the salt has been determined over the range 20–60°C.[4] Treatment of a solution of ammonium hydrogen sulphate with fluorine results in the liberation of ozonized oxygen and the formation of ammonium persulphate.[5]

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SECTION XV

AMMONIUM NITRATE

BY K. F. J. THATCHER

MANUFACTURE

Introduction

Ammonium nitrate does not occur in large natural deposits; hence, because of its commercial importance, considerable attention has been devoted to its manufacture. One report of its natural occurrence, together with other nitrates, in Turkestan, has been noted[1]; this is quite exceptional. Although ammonium nitrate is formed in suitable natural conditions (Mellor, II, 829), its high solubility makes deposition unlikely.

Whilst other methods have been suggested and some are operated, especially where the product is required for fertilizer use and a mixed salt product is acceptable, almost the entire world supply of this important salt is manufactured by direct synthesis from nitric acid and ammonia. The processes differ mainly in the manner in which reaction is effected. Care has to be exercised, as both reactants are volatile and the reaction is highly exothermic. The way in which the heat produced by the reaction is utilized to concentrate the salt solution formed, without causing losses through thermal dissociation, varies from process to process. The method of extracting and treating the solid product is important, because the salt is highly hygroscopic and after absorbing moisture it has a strong tendency to set into solid cakes which, once formed, are very difficult to break. The final product is usually submitted to a coating treatment to improve its storage properties. Since a number of serious explosions have been associated with ammonium nitrate, suitable precautions have to be taken to avoid this risk, for example, by limiting the amount of heated salt in the plant at any time, and avoiding contact between the hot material and organic matter with which it reacts vigorously.

Much of the following information on manufacturing processes is derived from patents. Many other patents relating to methods of producing this salt have been omitted, as they have little bearing on the chemistry of the processes.

A number of reviews have appeared of methods of ammonium nitrate production[2–7] including the sources of the raw materials. Frequently it is convenient to prepare both the ammonia and nitric acid required on the site where the salt is to be synthesized. Equipment for reducing the losses of ammonium nitrate in waste water has been described.[111]

Synthetic Processes

A number of manufacturing processes achieve the neutralization reaction in the liquid phase using gaseous ammonia,[5, 8–37] e.g., the Stengel[8] and Fauser[31–35] processes. A method which uses anhydrous liquid ammonia in a pressurized reaction vessel has been patented.[9] In one modern process[38] the ammonia is dissolved in recirculated mother liquor, and 60% nitric acid is then introduced to effect the reaction. A similar process using more dilute acid has also been patented.[39] Another recent patent relates to reaction conditions in which a small part of the nitric acid is in the vapour phase, thus giving ‘substantially anhydrous ammonium nitrate’.[40]

Reaction in the vapour phase can be employed,[41–47] but here some difficulty may be experienced in complete recovery of the mist formed in the reaction.[41, 48] The advantage of the gas phase reaction is that oxides of nitrogen with appropriate proportions of oxygen and water vapour can be mixed with ammonia to give the salt directly.[42, 45–47]

A similar method involves the catalytic oxidation of ammonia to oxides of nitrogen which can be absorbed in recirculated ammonium nitrate liquor. Ammonia is added to the recirculating solution between passes to neutralize most of the nitric acid formed, but the liquor is kept slightly acid.[49]

For the liquid phase reaction the usual method is to allow the dilute nitric acid to flow down a packed column and react with gaseous ammonia. The heat of neutralization, 20,600 kcal./mole,[8] causes some evaporation immediately and is also used to concentrate further recycled salt solution.[15, 19, 23, 25, 26, 29, 36] The rate of introduction of the reactants is adjusted so that a suitable operating temperature for the plant is reached. The actual temperatures attained vary considerably, but are such that the temperature is suitable for evaporation of water without causing decomposition of the product. Frequently there is a pressure drop between the reacting vessel and the evaporator, to assist in heat utilization[22–27, 29–33]; the reaction vessel itself is in some cases maintained above atmospheric pressure, while in others the evaporators operate under reduced pressure. This arrangement allows evaporation to be conducted at lower and consequently safer temperatures, but it has been shown that evaporation can still be economic at atmospheric pressure.[50] The concentration can be assisted by blowing air or other inert gas through the solution,[20, 21, 51, 52] and by agitation,[52, 53] as the heat liberated on crystallization of the salt is considerable. By these methods the concentration is generally raised to about 95% of molten salt, which is high enough for the subsequent graining process. Some methods claim that sufficient heat is liberated during the neutralization to obtain the salt without any external heat supply.[8, 19, 22, 38]

THE STENGEL PROCESS

Among the newest and safest processes of the neutralization type is the Stengel process.[8] The molten salt is continuously and rapidly removed from the reactor so that the total quantity in the system is relatively small. Ammonium nitrate of the desired water content can be produced in a single step. The neutralization takes place in a packed tubular reactor where streams of preheated nitric acid and ammonia vapour meet. The molten salt collects on the packing, flows to the bottom of the reactor and through a centrifugal cyclone separator. Here air is blown through to help to remove moisture, so that the liquid product flowing from the separator is ready for the graining process. Improvements in the process[54, 55] aim at obtaining material of lower moisture content directly. This is achieved by recirculation of the fines material with the nitric acid. The solution of the salt in the acid can then be safely preheated to higher temperatures, so that a product with less than 1% of water can be directly obtained. Other patents[56] claim that by passing the molten ammonium nitrate down a column against a counter-current of air, moisture contents as low as 0·2% can be achieved. Process data have been presented for the single-step manufacture of ammonium nitrate of various water contents by the Stengel process.[57]

Other Processes

FROM AMMONIUM SULPHATE

Some European processes depend on the double decomposition of two salts and subsequent fractional crystallization.[3] Those employing reaction of ammonium sulphate with calcium or sodium nitrate have been successfully operated for many years, whilst many other similar types of processes have been suggested, mostly in patent specifications.

In the reaction:

$$Ca(NO_3)_2 + (NH_4)_2SO_4 \rightleftharpoons CaSO_4 + 2NH_4NO_3$$

the equilibrium tends to give the products shown on the right-hand side, because of the low solubility of calcium sulphate. Use has been made of this reaction to form ammonium nitrate, after treating phosphate rock with nitric acid.[58] More attention has been given to the reaction between sodium nitrate and ammonium sulphate:

$$2NaNO_3 + (NH_4)_2SO_4 \rightleftharpoons Na_2SO_4 + 2NH_4NO_3$$

Although sodium sulphate is the least soluble component of the system, separation of ammonium nitrate is not easy, but it is achieved by fractional crystallization. A large excess of sodium nitrate influences the reaction in the required direction, as does the use of the most suitable temperature (55° to 65°)[59]; the use of a proportion of bisulphate has been reported to aid the method and also passing in gaseous ammonia to effect further separation of sodium sulphate either as such or as the double salt, $NaNH_4SO_4$, from which the ammonia can be recovered on heating.[59, 60] The use of a large excess of sodium nitrate in alcoholic solution was suggested in 1922,[61] and in fact the method was developed in Australia during the 1939–45 war.[62] A large excess of sodium nitrate at about 60° (138° to 145°F.) is treated with ammonium sulphate. Alcoholic extraction is then used to remove the ammonium nitrate and excess of sodium nitrate, which is in turn leached from the solution by a saturated solution of ammonium nitrate.

FROM AMMONIUM CHLORIDE

Methods of obtaining ammonium nitrate from the chloride have been used. The chloride solution is treated at the boiling point with excess of nitric acid in a counter-current apparatus; the gas and vapour leaving the system must be treated to recover nitric acid, hydrochloric acid, chlorine and nitrosyl chloride.[63–65] Ammonium chloride and 36% nitric acid can be caused to react at reduced pressure (20 mm. Hg), and heated by steam or hot effluent gases[66, 67]; again, the effluent gases are treated for recovery of nitric and hydrochloric acids. The equilibrium between ammonium chloride and sodium nitrate is not favourable for preparation of ammonium nitrate at low temperatures,[61] but can be employed if the solution is concentrated at 100°, and then, after adding a calculated quantity of water, it is cooled to 16°, when ammonium nitrate should crystallize.[68] The method was confirmed to work experimentally, but gave only 12·7 g. of ammonium nitrate from a solution containing one gram-molecule. Ammonium nitrate has also been produced on a commercial scale from calcium cyanamide.[104]

FROM CARBONATES OR CARBON DIOXIDE

Other methods have been devised for the manufacture of the salt using carbonates or carbon dioxide.[69–74] If the sodium chloride used in the Solvay process is replaced by sodium nitrate then ammonium nitrate and sodium bicarbonate are formed:

$$NaNO_3 + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4NO_3$$

This reaction eliminates the cyclic regeneration of the ammonia which instead has to be added in proportion to the quantity of sodium nitrate.[69, 70, 106] A concentrated solution of sodium nitrate is saturated with ammonia, then carbon dioxide is introduced while the solution is kept cool. The precipitated sodium bicarbonate is filtered off and solid sodium nitrate equivalent to the bicarbonate removed is added to the filtrate and dissolved. On standing, ammonium nitrate crystallizes and is removed by filtering; the filtrate is then recycled.[72] The ammonium carbonate recovered from the scrubbing liquor of coke-oven gas can be converted to ammonium nitrate by the use of nitric acid.[73] Nitrogen oxides can be absorbed in ammonium bicarbonate solutions and the resulting solution containing a mixture of ammonium nitrate and nitrite is oxidized to the nitrate by nitric acid (which could be made from some of the nitrogen oxides dissolved in water). Another similar method for the conversion of nitrous waste gases to ammonium nitrate has recently been patented.[112] A low temperature is preferable and an excess of ammonium salts is desirable to prevent the formation of free nitric acid.[74]

Production of Ammonium Nitrate Mixed with Other Salts

Ammonium nitrate is manufactured in large amounts mixed with other salts for fertilizer use. The method of manufacture of calcium nitrate–ammonium nitrate mixtures is to treat a suspension of calcium sulphate with ammonia and carbon dioxide, giving calcium carbonate and ammonium sulphate which are retained in the solution while it is treated with nitric acid, so that calcium sulphate is precipitated and a solution of calcium and ammonium nitrates remains.[75–78] An ammonium sulphate–nitrate mixture (Leuna saltpetre) is produced on a large scale from ammonium nitrate,[79, 80] but it can also be made by treating calcium sulphate with ammonia, carbon dioxide and nitric acid. The mixture must contain only a small excess of calcium sulphate, less than 5%, otherwise some ammonium sulphate is lost as a double salt with calcium sulphate.[81] Processes starting from phosphate rock have been suggested,[58, 82, 83] but the ammonium nitrate is formed by a similar method to that outlined above, from the calcium sulphate formed either from the action of sulphuric acid on the rock[82] or by leaching the rock with nitric acid and ammonium sulphate.[58, 83] Alternatively, after nitric acid treatment of phosphate rock, addition of ammonia gives ammonium nitrate mixed with calcium nitrate.[107] Solutions of aluminium nitrate, on boiling, precipitate a basic aluminium nitrate which can be treated with ammonia. The aluminium hydroxide is filtered and ammonium nitrate recovered from the solution.[84]

Electrolytic Methods

Two electrolytic methods have been proposed for making ammonium nitrate. Both require a diaphragm cell; one starts from nitric acid[85] and the other from ammonia.[86] The ammonia is oxidized in a two-compartment cell with an asbestos diaphragm and an iron anode in a solution containing 16% of ammonium carbonate with copper hydroxide as a catalyst. The cathode solution is potassium hydroxide. Extra ammonia is passed in as the electrolysis proceeds to keep the pH at 8·42. An efficiency of 75% for the conversion from ammonia to ammonium nitrate is claimed.

Miscellaneous Processes

Ammonium nitrate can be formed by heating ammonia, carbon dioxide and air above the temperature of decomposition of ammonium carbonate and passing the gas into ammonium nitrate solution, giving ammonium carbonate in solution. This is decomposed by addition of nitric acid, recovering the ammonia as ammonium nitrate. This method is intended for recovery of the gases used in synthesizing urea.[87] Similarly, ammonium sulphite solution can be decomposed under reduced pressure by nitric acid to recover ammonium nitrate.[88] Ammonium nitrate is also obtained as a by-product in the treatment of phosphate rock with nitric acid. After the calcium and magnesium carbonates are precipitated by ammonia and carbon dioxide, the filtrate contains up to 20% ammonium nitrate.[89] The recovery of the salt from waste explosives by aqueous extraction has also been used to obtain supplies.[90] Another patented process starts from hydrogen and oxygen obtained by electrolysis of water.[105] The oxygen and air can be caused to react in the presence of a platinum catalyst to give nitric acid. The waste gas from this step and the hydrogen from the electrolysis can be used to make ammonia, after removing the oxygen in the waste gas by combustion with a part of the hydrogen. Part of the ammonia is then oxidized to nitric acid before neutralization to ammonium nitrate.

Ammonium nitrate is among the products obtained when many other nitrates are reduced by hydrogen in a silent electric discharge.[91] A solution of nitric acid in diethyl ether, which had been contaminated with oxides of nitrogen, deposited crystals of ammonium nitrate on standing.[92] Ammonia gas reacts with magnesium nitrate, $Mg(NO_3)_2,2H_2O$, giving a mixture of ammonium nitrate and magnesium hydroxide. The reaction occurs with a solution or with the fused salt; the reaction is of the double decomposition type and reaches a state of equilibrium.[93]

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Preparation and Treatment of Solid Ammonium Nitrate

Most production methods give a concentrated (90–95%) hot solution from which the solid ammonium nitrate is prepared. This process is termed graining. For its major uses the size range and physical condition of the salt particles are both important.

One of three methods is normally employed to obtain granules of the appropriate size range.[94, 95, 96] The older method is to use batch evaporation of the solution with carefully controlled stirring and cooling.[94–96, 108, 109] Prilling is a newer method which can be used with solutions of at least 95% concentration.[10, 95–97, 98, 108] The molten salt is sprayed down a tower, similar to a shot-tower, against a countercurrent of cool air. The salt reaches the bottom as smooth spherical particles about $\frac{1}{16}$ in. in diameter. The prilled ammonium nitrate is improved by introducing a small quantity of ammonia before prilling.[110] Another modern method, associated with the Stengel process, is to spray the hot concentrated ammonium nitrate solution on to water-cooled stainless steel belts.[96, 99] The solidified sheet so formed is broken up to the desired size range. The material which is too fine can be dissolved and recycled.

Because of its high hygroscopicity and caking propensity the crude ammonium nitrate from the various processes is treated to ensure that the product is in a saleable and usable state. Whilst the problem is by no means fully understood, caking is very sensitive to the amount of moisture in the material and seems also to have some connection with the changes of phase which can occur in the crystalline salt. The result is the formation of salt bridges between the particles, setting the mass to one solid cake which is very difficult to break. Anti-caking treatments have been reviewed[100] and many have been patented.

The methods used are designed either to prevent moisture uptake[101] or to modify the crystal structure or habit.[102, 103] The former type of treatment involves coating the salt granules with a hydrophobic film which may consist of a paraffin-type material, organo-silicon halide, resin or other water-repellent substance; sometimes an inert powder such as clay, kieselguhr, kaolin or alumina is used in addition to improve the free flowing characteristics of the product. The crystal structure can be improved by carefully controlled conditions during drying or by adding inorganic materials to stabilize the desired crystal phase.[102] The crystal habit can be modified by certain dyes, generally of a sulphonated type[103]; acid magenta is one of the most effective of those tried. If a dye is used, the concentration need be only about one part in a thousand, but for an inorganic additive to be effective a few % of it must be introduced.

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PHYSICAL PROPERTIES OF AMMONIUM NITRATE

Crystal Habit and Structure

Much more is now known about the structure of the different crystal modifications of ammonium nitrate mainly as a result of *X*-ray analysis, although other methods have also helped.[1–3] The crystal habit can be changed by the presence of small proportions of many foreign ions[4, 5] and of dyes.[6–8] The effect of dyes has been studied in detail by Whetstone,[6–9] who found that the modifying properties of many dyes were related to their anionic and cationic polar substituents. The positions of the polar substituents in the dye were critical in defining its habit-modifying power and the solubility of the dye in the salt solution was also critical. If a planar dye molecule can be so superimposed on planes representing the edges of the growth layers that a sufficient proportion of its polar groups falls on positive or negative centres, then adsorption takes place. Hence it is important to have a planar grouping of the polar groups in the dye structure if it is to function in modifying crystal habit. The adsorbed dye then obstructs growth until it is dislodged or overgrown. Acid magenta was found to have the strongest influence on ammonium nitrate and to reduce its caking tendency.

The rate of crystallization of ammonium nitrate from solution is proportional to the degree of supersaturation until the point is reached where spontaneous crystallization occurs.[10] The rate of growth is greater (by about 20%) on individual crystals which are under strain. This supports the theory that growth of crystals is normally dependent on the propagation of dislocations.[11]

A study of crystal overgrowth of the salt on the cleavage plane of mica has shown the relationship of the different planes of the crystal lattice; as the transitions occur cracks appear in the crystal film in varying directions.[1] The same relationships have been investigated by the *X*-ray method, a single crystal being maintained in a fixed orientation and the diffraction pattern it gives recorded at various temperatures.[12] The crystal types of the five solid phases existing at normal pressure are phase I, cubic; phase II, tetragonal; phase III, orthorhombic I; phase IV, orthorhombic II; phase V, hexagonal (or possibly only pseudo-hexagonal[13]). Values of the cell parameters and probable space groups are given in Table I. Where more than one value is given, that preferred is given first.

Table I.—Data on Crystal Structure of Ammonium Nitrate

Solid phase	Space group	Unit cell dimensions, A.			Other information	Ref.
		a	*b*	*c*		
I	$Pm3m$	4·40	—	—	at 155°, one NH_4NO_3 in unit cell	13
II	$P_{\bar{4}}-2_1m$	5·74	—	5·00		14
II		5·75	—	5·00	two NH_4NO_3 in unit cell	13
III		7·18	7·71	5·83	above 32°	15
III	$Pbnm$	7·14	7·65	5·83		16
III	$Pbnm$	7·06	7·66	5·80 ± 0·03	four NH_4NO_3 in unit cell	13
IV		5·757	5·451	4·935	at 24°	15
IV	$Pmmn$	5·75	5·45	4·96	two NH_4NO_3 in unit cell	13
IV		4·92	5·43	5·73		17
V		5·75	—	15·9	six NH_4NO_3 in unit cell; samples at −33° and −78° identical save for displacement due to expansion	13

As the temperature is lowered and the phase transitions occur, the nitrate group, which is planar, loses some degrees of freedom. In phase I the *X*-ray pattern shows that the nitrate group has spherical symmetry,[13, 18, 19] as in other high temperature cubic modifications of alkali nitrates.[18, 20] At lower temperatures the rotation is only about an axis perpendicular to the nitrate plane.[20] This rotation is reduced to torsional oscillation at the lower transition points.[13] The transition between phases III and IV is a true change in structure although both are orthorhombic, with a change in the co-ordination number.[19] The phase V to phase VI transition is attributed to rotation of the ammonium groups.[19] The Raman spectrum of phase IV ammonium nitrate suggests, however, that the ammonium ions are not in a completely disordered arrangement.[21]

A simplified picture of the structure of the ammonium nitrate/nitric acid complex, NH_4NO_3–$2HNO_3$, obtained from *X*-ray data, is that it consists of sheets containing NH_4^+ and NO_3^- ions separated by HNO_3 molecules, two nitric acid molecules being joined by hydrogen bonds to each nitrate ion.[22]

Solubility

SOLUBILITY IN WATER

Ammonium nitrate is extremely soluble in water, the solubility rising rapidly with increasing temperature as shown in Fig. 1. The values quoted in Table II are taken from Hoeg,[23] whose work covers the range from room temperature to the m.p. of the salt, and from the most recent determination[24] in which the solubility was determined at 5° intervals. Table II also includes values given by Cohen and Bredée[25] and by Millican *et al.*[26]; the last figures are slightly higher than those of the other authors, which show close agreement. The solubility at temperatures above 100° was found by observing the temperature at which a known weight of ammonium nitrate completely dissolves.[27] Schröder's equation for the solubility of salts was found to predict the solubility of ammonium nitrate above 70°, but at lower temperatures solubility is higher than the ideal.[28] Agreement with theory is best at high temperatures and shows that compound formation can occur to only a very small extent in the system. Behaviour close to that for an ideal solution has been reported for concentrated solutions at high pressures.[29] Ammonium nitrate readily gives supersaturated solutions, from which spontaneous crystallization does not occur at less than about 10% supersaturation.[30]

The effect of increased pressure is to reduce the solubility of the salt.[29, 31] At 25° and atmospheric pressure the saturated solution contains about 67% of the salt, but when the pressure is raised to 10 kilobars the concentration falls to about 30%.[31] The influence of nitric acid on the aqueous solubility has been studied,[32] and the solubility curve shows a minimum with changing acid concentration at temperatures below 30°.

Table II.—Solubility of Ammonium Nitrate in Water

Temperature, °C.	Specific gravity[23]	Density g./ml.[24]	Wt.-% of ammonium nitrate in solution			
			23	24	25	26
20	1·3115	—	66·1			
30	—	1·3295	69·9	69·86	69·9	70·1
40	1·3415	1·3449	73·3	73·58	73·7	74·2
50	—	1·3586	76·8	76·99	77·0	77·8
60	1·3519	1·3713	80·2	80·14	—	80·7
70	—	1·3818	83·2	83·20		83·5
80	1·3940		85·9			
100	1·4145		91·0			
120	1·4260		94·7			
140	1·4320		97·4			
160	1·4360		99·4*			
170	1·4370		100·0*			

* Values obtained by extrapolation

The solubility curves of ice VI and ammonium nitrate IV have been calculated[29]; the solubility decreases rapidly at increased pressure.

SOLUBILITY IN NON-AQUEOUS SOLVENTS

Unlike most other salts ammonium nitrate shows considerable solubility in many organic solvents as well as in other non-aqueous solvents such as ammonia.

In water–ethanol mixtures the solubility is not greatly reduced until the alcohol concentration exceeds 40%. The change of solubility with temperature and with composition of the solvent is shown in Fig. 1 which is based on data of Thompson and Vener.[24] Two liquid phases can exist at temperatures above 65·7°, the upper phase rich in ethanol, the lower rich in ammonium nitrate. Solubilities in the richest ethanol mixture, with 93% of alcohol in the solvent, are shown in Table III. The salt is soluble also in other alcohols. Stark and Gilbert have used solutions with concentrations up to 0·9 M. in methanol.[33] Solutions of the salt in methanol have also been used for viscosity measurements.[34] Solubility isotherms at 30° for the water–methanol–ammonium nitrate system have been given.[35] In aqueous *iso*propanol mixtures, the saturated solution gives two liquid phases over a very large region in the temperature range studied, viz., 25° to 75°.[36] Separation into two phases occurs at concentrations from about 15% of the alcohol in the solvent up to about 90%, with no evidence of a plait point. Solubility in the 95% *iso*propanol mixture is given in Table III, together with the densities of the saturated solutions.

Table III.—Solubility of Ammonium Nitrate in Ethanol and iso*Propanol*

Temperature	92·6% Ethanol[24]		95·6% *iso*Propanol[36]	
	Wt.-% of Ammonium nitrate	Density g./ml.	Wt.-% of ammonium nitrate	Density g./ml.
25	7·29	0·8382	—	—
30	8·07	0·8377	3·23	0·8025
40	9·72	0·8372	3·81	0·7962
50	11·65	0·8375	4·59	0·7902
60	13·91	0·8385	5·45	0·7848
70	16·69	0·8435	6·37	0·7817
75	18·19	0·8407	6·89	0·7806

Ammonium nitrate is said to be miscible with mannitol, resorcinol, urea and acetamide in the liquid state, and to show some solubility in phenylenediamine, picric acid, cholesterol and trinitrotoluene.[37] In pyridine the solubility of ammonium nitrate is given as 22·88 g. of salt per 100 c.c. of solvent at 25°C.[38]

Solutions in anhydrous hydrogen cyanide[39] and in anhydrous acetic acid[40] have been studied. The solubility curve in anhydrous acetic acid, which is of very unusual shape, is reproduced in Fig. 2; two points of inflexion occur at 60 mol.-% and 85 mol.-% of solute.[40] The break in the neighbourhood of 125° may possibly be associated with the crystal transition at this temperature. The solubility in anhydrous acetic acid increases in the presence of silver nitrate, possibly by formation of a double salt.[234]

The solution of the salt in liquid ammonia has been previously described in detail (Mellor II, 844) and is known as Divers' liquid. Further data are now available for this solution.[41–44] From −50° to −34° the solubility changes from 70·1 g. to 77·9 g. of salt per 100 c.c.[43] The saturated solution at 25°C. contains 79·6 wt.-% of the salt; in molar quantities this represents 0·829 moles of salt per mole of ammonia, whereas for the saturated aqueous solution there is 0·482 mole per mole of solvent.[42] The solubility is thus reduced as water is added to the solvent. A graph of the change in solubility with solvent composition at 25° has been constructed.[42]

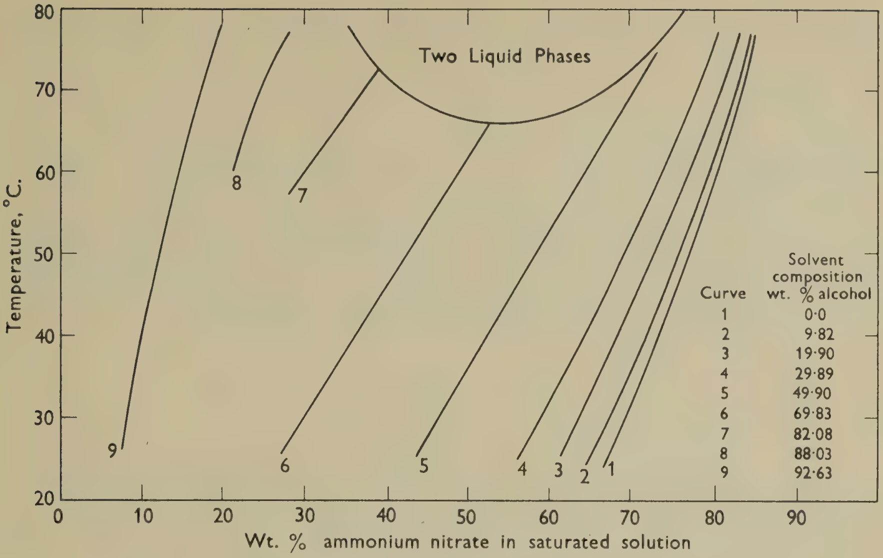

FIG. 1.—Solubility of ammonium nitrate in aqueous ethanol

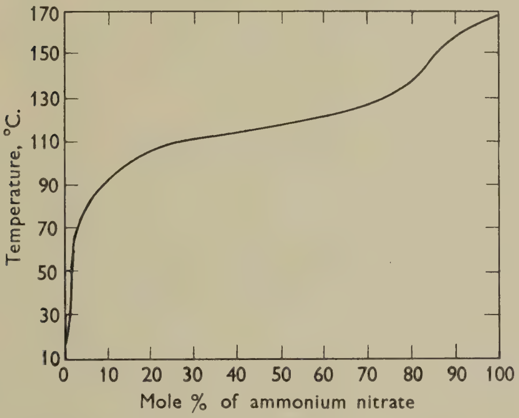

FIG. 2.—Solubility of ammonium nitrate in anhydrous acetic acid

Hygroscopicity

In common with several other salts highly soluble in water ammonium nitrate is extremely hygroscopic, but no hydrates are formed with the simple salt.

At temperatures up to 20° no absorption could be detected with air below 84% humidity, but as the humidity increases the absorption rate becomes rapid until dissolution of the salt occurs.[45] At 25° absorption starts at from 55 to 67% relative humidity of the air, according to the form of the ammonium nitrate.[46] The moisture absorption rate does not vary for initial moisture contents of the salt between 0·5 and about 30%.[47] The actual rate of moisture absorption, measured for samples of ammonium nitrate stored over sulphuric acid of different concentrations, is inversely proportional to the acid concentration.[48] The relationship between vapour pressure and hygroscopic properties has been discussed.[49]

Modification III of ammonium nitrate is said to be less hygroscopic than any of the other modifications,[45] and may be rendered non-hygroscopic by first liquefying it by the action of anhydrous ammonia and then removing the ammonia by evaporation below 15°.[50] When ammonium nitrate is stored in bulk the moisture absorbed from the air gradually spreads through the heap,[51, 52] but when the material was placed on a damp surface the moisture only rose about 15 cm. into the heap.[51] In practice the granular material is more hygroscopic than powdered ammonium nitrate,[52] unless it has been given a protective coating (see page 510). The reason for the lower hygroscopicity of powdered material, in bulk, is that it soon becomes coated with a caked layer or crust which prevents access of more air and moisture.[52] The hygroscopicity can be reduced by adding certain other salts such as potassium or ammonium phosphate, sulphates and chlorides[45, 52]; powdered limestone can also be used,[53] but it must be fairly coarse to reduce nitrogen losses.

Density

A recent measurement of the density of this salt gave a result of 1·72 for the phase IV form,[17] which agrees with the values of Behn and Retger (Mellor, II, 831). The density of the molten salt has been measured between 170° and 210°.[54] Hoeg's values for the specific gravity of aqueous ammonium nitrate[23] show good agreement, in general within 0·5%, with those given previously (Mellor, II, 831), but they cover a wider range of temperature and concentration. The density of aqueous solutions of the salt has been measured with a high degree of accuracy on a number of occasions in connection with other studies.[24, 55–58] Accurate values covering a wide concentration range at 25° [55, 56] and 35° [55] are given in Tables IV and V respectively. For comparison the values calculated from the equation derived by Gucker,[59]

$$d_4^{25} = 0{\cdot}997077 + 0{\cdot}032628c - 9{\cdot}63 \times 10^{-4}c^{3/2} - 4{\cdot}73 \times 10^{-5}c^2$$

where c is the concentration as molarity, are also given and show good agreement with those found experimentally. A simpler equation, $d = d_w + 0{\cdot}0044c$, where d_w is the density of water at temperatures from 40–80°, gives the density, d, of solutions of ammonium nitrate of concentration c in wt.-% at the chosen temperature.[60]

The densities of saturated aqueous ethanol solutions have been measured[24] and also those of aqueous *iso*propanol mixtures.[36] A few of the values are included in Table III. Values for the density of methanol solutions at 25° are given, with the apparent molar volume in that solvent,[33] in Table XI (see p. 530).

At 15° the densities of ammonium nitrate solutions in liquid ammonia are 0·654 for a solution containing 6·76 g. of salt per 100 g. of ammonia and 0·744 for one containing 27·46 g. of salt.[61] At 25° a density of 1·212 g./ml. is found for the saturated solution,[42] and in another study densities ranged from 1·000 at −25° to 1·178 at 20°.[62]

The density of solutions of ammonium nitrate in mixtures of water and ammonia rapidly decreases with increasing ammonia concentration.[63]

The variation in density of solutions of ammonium nitrate with temperature shows changes in direction in the region of 32° corresponding with the crystal transition, but the change occurs at somewhat lower temperatures for dilute solutions.[64]

Plasticity and Compressibility

The plasticity of ammonium nitrate crystals has been studied in some detail.[65, 66] Bond[65] found that the freshly crystallized needle-shaped crystals, which generally separate from an aqueous solution, could easily be bent by the fingers provided the force is not applied too suddenly; if a fixed load is applied to a horizontally mounted crystal the initial rate of bending is greatest. The rate of bending, however, increases much more rapidly than the applied force. The changes in crystal structure resulting from the bending are very slight when judged from changes in the optical properties. The probable changes in internal structure have been discussed, and calculation shows that the pseudo-viscosity of the salt is of the same magnitude as for glacier ice. Crystals subjected to plastic deformation do not regain their original shape.[67] Addition of ammonium sulphate to ammonium nitrate strongly reduces the plasticity of the mixture.[68]

The flow pressure of ammonium nitrate depends on which of the polymorphous modifications of the salt are present.[66] The flow pressure of dried ammonium nitrate shows a slow linear decrease up to the transition point at 32·1°, where there is a drop, followed by a more rapid linear fall as the temperature is further raised. The rate of change is, however, influenced by the prior treatment of the sample. A sample which has been rapidly cooled to $-15°$ shows a more rapid change in flow pressure up to 32·1° and a slower change at more elevated temperatures. The region where there is a rapid change in flow pressure corresponds to conditions where the salt is wholly or partly in a metastable state. Therefore it seems possible that the effect is in part due to the unstable state and that increased pressure induces the change to the stable condition. A sample cooled slowly to room temperature had a flow pressure of 5390 kg./sq. cm., whereas it was only 1773 for a sample rapidly cooled to $-25°$, which would probably contain a mixture of phases III, IV and V.

The cubic compressibility of ammonium nitrate has been measured at pressures up to 100,000 kg./sq. cm., at intervals of 10,000 kg./sq. cm. or less.[69] The decrement $\Delta V/V_0$ for the 0–50,000 range is 0·162 whilst for the 50,000 to 100,000 interval it is only 0·061. It has been suggested that as the load–volume curves for ammonium nitrate are similar to those obtained with lead shot (where the result of compression is deformation of the particles), a similar change occurs with the salt.[70] In view of its plasticity this does not appear impossible. The equation $10^5k = 668{\cdot}9p - 13{\cdot}86p^2$ has been given to describe the bulk compression, k, of the salt at pressures, p, from 1 to 12 kilobars.[71] Solid ammonium nitrate does not show any tendency to decompose when subjected to pressures of up to 50,000 kg./sq. cm. together with shearing stresses up to the point of plastic flow.[72] The compressibilities of the several modifications of the salt differ and have been investigated[73, 74]; under increased pressure the change from form III to form IV may occur at temperatures as high as 50°.[73]

For aqueous solutions of ammonium nitrate the compressibility has been measured at 20°.[75, 76] The variations fit the equation $\phi(K_2) = \phi(K_2^0) + C\sqrt{c}$, where $\phi(K_2)$ and $\phi(K_2^0)$ are the molal compressibilities of the solution at concentration c, and infinite dilution, respectively; the constant C has a value 2·2 for ammonium nitrate and $\phi(K_2^0)$ is $-11{\cdot}4 \times 10^{-10}$ in c.g.s. units.[75] If the molal compressibility is obtained by summation of the ionic values, the value 11·7 is obtained. The compressibilities of solutions where c is 0·9999, 0·5000, 0·2500, and 0·1250 are 9·19, 9·84, 10·1 and 10·4, respectively.

When aqueous solutions of ammonium nitrate are subjected to increased pressure, the partial volume of the salt decreases with increase in pressure, except for a slight initial rise with 15 wt.-% or less of salt. Above five kilobars the partial volume is independent of concentration and the partial compressibility is close to that for the solid.[29]

The compressibility of mixed solutions, molar with respect to lead and ammonium nitrates, shows minima in the compressibility–concentration curves suggesting complex formation.[77]

Viscosity and Fluidity of Solutions

The accurate data of Campbell and Kartzmark cover a wide range of concentration for aqueous solutions at 25° [55, 56] and 35°,[56] and at 95° for solutions up to 15 M.[58]; they also give temperature coefficients for the fluidity of the solutions. A selection of their results is given in Tables IV and V. The viscosity of solutions has been measured at 180°; the relative viscosity of the molten salt at this temperature is 10·1.[78]

Table IV.—Density and Viscosity Data for Aqueous Ammonium Nitrate at 25°C.

Concentration, molarity	Density in g./ml.		Viscosity, centipoise	Fluidity, rhes
	Exptl.	Calc.		
0·000	0·99707	0·99707	0·8937	111·9
0·0540	0·99883	0·99883	0·8924	112·0
1·0261	1·02957	1·02957	0·8635	115·8
1·7009	1·05028	1·05029	0·8564	116·7
1·9184	1·0567	1·0569	0·8561	116·8
2·4611	1·0735	1·0734	0·8604	116·2
3·9940	1·1190	1·1187	0·9005	111·1
5·5346	1·1637	1·1636	0·9846	101·6
7·7100	1·2251	1·2252	1·1200	83·35
10·8027	1·3100	1·3098	1·8820	53·13

Table V.—Density and Viscosity Data for Aqueous Ammonium Nitrate at 35°C.

Concentration, molarity	Density in g./ml.	Viscosity, centipoise	Fluidity, rhes
0·000	0·99406	0·7225	138·4
0·0538	0·99575	0·7222	138·5
1·0234	1·0269	0·7119	140·5
1·9104	1·0523	0·7132	140·2
3·9749	1·1136	0·7639	131·0
7·6705	1·2188	1·0325	96·85
10·749	1·3035	1·6139	61·96

The viscosity of dilute solutions actually decreases slightly to a minimum value at about 2 M. concentration at 25°, but increases as the concentration becomes greater. At 35° the minimum viscosity is at about 1·7 M., but at 95° there is no evidence of such a minimum although the viscosity increases only very slowly at low concentrations.

Values for the viscosity of aqueous solutions are given by other investigators.[79–83] Rabinowitsch measured the relative viscosity at 100° for solutions containing up to 87% of the salt; it appears to increase rather more rapidly at concentrations above about 60% of the salt, but at lower concentrations is proportional to concentration.[81] The relative viscosity was reported to decrease with increasing temperature[34]; but, as can be seen from the Tables, it is also dependent on concentration.

Supersaturated solutions do not show any sharp change in viscosity when the supersaturated condition is reached.[80] The plot of the reciprocal of temperature against the logarithm of the viscosity gives a straight line at low concentrations only.[80] The specific viscosities of solutions in liquid ammonia and in water are similar; they are independent of pressure and show little variation with change of temperature. In both cases they are directly proportional to concentration at the low concentrations studied.[83] The relative viscosity of methanol solutions of ammonium nitrate decreases with increasing temperature.[34] Viscosity data of aqueous solutions of mixtures of lead nitrate and ammonium nitrate afford evidence for the existence of the complex ion $Pb(NO_3)_4''$.[82]

The relative viscosity of ammonium nitrate solutions in liquid ammonia at temperatures of −64°, −54° and −44° is proportional to the concentration, for the limited range studied, in which it does not vary with temperature.[83]

Phase Transitions

TRANSITION TEMPERATURES

The original account (Mellor, II, 833–6) shows that earlier investigations devoted much attention to the phase transitions of this salt, because they showed certain unusual, if not unique, effects. Some of these studies are as comprehensive and accurate as any that have followed since; especially notable is the work of Bridgman who made an extensive study of the effect of pressure on the stable regions of the various modifications. He found that phase III ceases to exist at pressures above 860 kg./sq. cm., and also discovered a new phase, VI, stable only at pressures above 9000 kg./sq. cm., replacing phase II as intermediate between phases I and IV at those pressures.

The accepted value for the melting point of ammonium nitrate, 169·6°C., is that previously quoted. It is, however, very sharply affected by the presence of moisture; 1% lowers the melting point by 11·5°C.,[26] and as the salt is exceedingly difficult to bring to complete dryness, low values have occasionally been reported. As recently as 1941 Dingemans found the melting point to be 169·1° after the sample had been dried for five months,[84] and Kretzschmar gave the melting point as 169·0°.[85] The effect of various foreign ions on the melting point has been investigated.[86] The cryoscopic effect of other nitrates as solutes has also been tested.[87] Both water and nitric acid, or a mixture, cause a cryoscopic lowering of the melting point.[88] The transition points for the various solid phases of ammonium nitrate have been studied on numerous occasions.[1, 2, 12, 13, 16–18, 20, 66, 73, 74, 89–114, 237]

The very slow rate of transformation from one crystal form to another, and its dependence on the previous history of the sample, has led to some disagreement as to the true transition temperatures, in particular for those at lower temperatures where change is slowest. The phase changes in the solid state rarely take place at the true equilibrium temperature; there is generally a slight lag or hysteresis effect. Representative values may be given as:

Phase	liquid	↔	solid I	↔	solid II	↔	solid III	↔	solid IV	↔	solid V
			ϵ		δ		γ		β		α
Transition temperature, °C.		169·6		125·2		84·2		32·3		−18	

Transformations at lower temperatures have been reported. An anomaly in the specific heat was found between −57° and −65°; differential thermal analysis confirmed this transition and indicated another transition in the region −150° to −160°.[92, 94] Crenshaw and Ritter also found a sharp rise in specific heat at about −60° and gave the transition temperature as −60·4° with a heat change of 530 g.-cal./g. mol. for the conversion.[115] More recent work confirmed the existence of the lowest transition point (below −170°), but not that at −60°.[91, 116]

The transitions at 125·2° and 84·2° are, however, well established and there is general agreement that these are the best values. Even here the temperatures given are the mean of those found for the transition point on heating and cooling. The temperature 32·2° is given by several authors for the change-over point between phases III and IV[95, 100, 107, 109, 117]; other values reported are 32·1°,[66, 73, 89] 32·3°,[114] 32·5°[12] and 31·8°.[112]

From measurements of the change in concentration with temperature for the two forms in a saturated solution, a true transition temperature of 32·27° is indicated, where the two concentrations coincide.[25] From the latest investigation it appears that the true transition temperature depends on the proportion of the two phases present; it lies between 32·22° and 32·30°.[118] The conversion between phases IV and V has also been said to occur at −16°.[90]

On cooling it is possible to transform phase II directly to phase IV at about 50°,[12, 90, 91, 93, 96] or at 45° according to Fukuyama,[105] or at 55° according to another recent study.[19] This metastable transition can be made to occur only when the sample has been maintained in the second phase for a sufficient time to ensure conversion of all the phase III nuclei to the new state. This requires several hours heating at a temperature of 85° or higher. The metastable change is said to be shown better by moist specimens of the salt[93, 117] and also to be more easily observable with single-crystal specimens.[114] At this point the specific heat is reported to vary by

160 g.-cal./degree/mole,[96] but it seems more probable that this is meant to be the value for the heat of transition.

RATES OF PHASE CHANGES

The kinetics of the rate of the phase changes have been used to determine the true transition temperatures.[89, 95, 99, 100, 108, 109, 111, 118] The rate of the transformation is proportional to the difference between the true change-over temperature and the temperature at which conversion is occurring. This feature has been shown to apply only over a limited temperature range.[109] Early and Lowry[89] were the first to use this method to determine the 32·1° transition; it was the mean of the temperatures, on either side of which the rate was the same. The rate of transformation is not, however, a linear function of temperature difference.[99, 118] The rate at 32·1° itself was not measurable.[89] More recent investigators found that there is an equilibrium for the change from phase IV to phase III at 32·3°.[95]

For the kinetics of the transformation from phase IV to phase III the following equation for the degree of transformation α, has been proposed:[111] $\alpha = 1 - e^{-ktn}$, where t is time and the constant n has a value of about 3 if the modification IV is kept at room temperature for several hours previous to the experiment. But n is only about 2 if the sample has been kept below the transition temperature for a short time, less than 4 hr. In the first case all the nuclei for form III must form during the experiment, whereas in the second case there are sufficient nuclei remaining from the previous heating to ensure conversion. The rate of transformation is small for samples which have not been previously heated above the transition temperature, but can be increased during the first few cycles by repeated heating and cooling for a few minutes, but then the rate reaches a constant value.[111, 118] The rate can also be increased about threefold by grinding the ammonium nitrate, probably owing to the formation of a greater surface area and more dislocations, which increase the number of conversion centres available.[109, 111] A similar result is achieved by recrystallization into small crystals.[111] The conditions for the persistence of nuclei of the metastable phase at temperatures away from the true transition temperatures and suggestions for their shape and mode of growth have been discussed.[118] Attention has been drawn to the importance of these transformation centres.[238]

The effect of the physical condition of the material under investigation indicates the limitations of the kinetic method. The rate is also affected by the presence of moisture, which again accelerates the change,[109] although it is said not to affect the temperature of transition.[119] As the grain size changes during conversion[120] it is not permissible to use the same sample repeatedly. Owing to the influence of the previous history of the sample, it is difficult to reproduce results.

VOLUME CHANGES DURING PHASE TRANSITIONS

As the transitions are accompanied by a volume change they have been followed by the dilatometer method (e.g. [89, 95, 108, 118]), generally with toluene as the dilatometer fluid. The progress of the transformation gives an S-shaped curve, which conforms to a formula developed for autocatalytic processes.[108] Early and Lowry[89] found the hysteresis of the 125·2° transition to be 0·05° (mean) with extreme temperatures at 125·00° on cooling and 125·38° on heating. Connel and Gammel[110] found the hysteresis effect to be 0·3° for the conversion between phases I and II and 0·7° between phases II and III. The extent of the lag is of course dependent on a number of physical factors, e.g. rate of heating or cooling and the particle size, and so is not comparable among various workers. Because of this lag the transition temperatures given by differential thermal analysis are somewhat higher than the accepted values.[113]

The transition point at 32·1° is accompanied by the largest volume change as modification IV has the smallest molecular volume, and III has the largest. The fractional change for complete transformation is 0·0221 c.c./g.[98] This value is about 9% higher than that of Bridgman, possibly because the change was incomplete in his case. A volume change of 6·5% was reported,[74] but this work has been criticized.[101] The values for the atomic volumes for the two forms near the transition point are 0·60465 for phase III at 33·5° and 0·58250 for phase IV at 32·0°.[98] Because of the large volume change the transition point is sensitive to pressure changes; the more recent data[73, 74] are not in agreement with earlier findings (Mellor, II, 835) and appear to be in error.[101] When the change in specific volume was estimated by a pycnometer method it was smaller than when it was done by a dilatometer method.[121] The specific volume of modifications III and IV increased on repeated heating and cooling cycles.

STABILIZATION OF THE PHASES

The various crystal modifications of ammonium nitrate can be stabilized by the addition of some foreign substances, which may be inorganic salts or certain dyes. Interest in this direction has generally been aimed at preventing caking of the salt during storage and many patents have been taken out in this connection (see page 510). One of the causes of caking is thought to be phase changes occurring in the stored material. Some evidence to this effect is found in the influence of potassium nitrate on the caking of the ammonium salt.[122] Samples with higher proportions of the potassium salt cake at lower temperatures, and only when they are stored below the temperature for the phase III to phase IV transition for the sample. The caking is also a function of moisture content; it increases fivefold when the moisture changes from 0·45 to 0·9%, but it is not influenced by further increase in the moisture content. Caking can be affected by the treatment of the ammonium nitrate itself.[123]

One or two per cent of the following additives stabilize the cubic phase I: cæsium chloride, sodium fluoride, ammonium chloride (but not ammonium iodide).[106] For the tetragonal phase II, sodium nitrite, potassium perchlorate, silver sulphate and cæsium nitrite are effective[106]; and for the orthorhombic phase III, potassium permanganate, potassium chlorate, potassium fluoride, lead chloride ($PbCl_2$) and potassium iodide can be employed[106]; the use of potassium nitrate has been patented.[107] The potassium nitrate can form solid solutions with phase III ammonium nitrate containing considerable quantities of potassium nitrate; according to its quantity the range of stability of phase III is extended.[124] Addition of various cations, K^+, Cs^+, Tl^+, which form solid solutions with ammonium nitrate generally lowers the transition temperatures; rubidium, however, with the same ionic diameter as the ammonium ion, has no effect on the transitions.[19] The true transition temperatures are not affected by the presence of moisture,[125] nor are they affected by salts such as calcium carbonate which do not form solid solutions.[126] The apparently large change in transition temperature which is caused by the presence of only about 1% of potassium nitrate could be due to inhomogenity; the solid solutions near the surface of the crystals being rich in potassium prevent surface nucleation to commence the formation of modification IV.[127] Larger amounts of potassium nitrate, 8–10%, lower the transition temperature to $-20°$.[236]

The effect of the various salts was studied microscopically on mica cleavage surfaces. The stabilization does not seem to depend on the ability of the impurity itself to give an oriented overgrowth on mica, as some of the effective salts do not themselves give oriented overgrowths, nor does any chemical analogy between the additive and ammonium nitrate appear necessary. The impurity does not require the same general symmetry of space lattices, but stabilization occurs when two sets of dense plane cells coincide dimensionally within the limits usually acceptable in oriented overgrowth.[106, 128]

The effect of a supersonic field on the polymorphous transitions has been studied.[235] A sufficiently strong field was found to be capable of reversing the direction of propagation of the two higher transitions, but not that at 32·1°. The phenomenon was probably due only to the mechanical effect of the supersonic wave. As the phase transitions in the solid state occur the grain size alters. The number of grains per unit area increased from 2 to 36 during transformation at 87°.[120]

Vapour Pressure

SOLID AMMONIUM NITRATE

The vapour pressure of solid ammonium nitrate is due to both thermal dissociation and chemical decomposition:

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3; \qquad NH_4NO_3 \rightarrow N_2O + 2H_2O$$

At lower temperatures the pressure produced is due almost entirely to thermal dissociation, and recombination occurs on cooling. However, as the temperature is raised above about 190°, decomposition occurs,[129] mainly according to the reaction given above. The dissociation pressure has been measured by a method which avoids measuring the pressure due to the decomposition products, the effect of which was calculated to be less than 1% even on the highest reading.[129] The dissociation pressures in mm. Hg are at 188·2°, 3·25; at 205·1°, 7.45; at 215·9°, 11·55; at 223·1°, 15·80; at 236·7°, 27·0; at 249·1°, 41·0. For temperatures above 250° the dissociation pressure, p cm., has been estimated from free energies based on extrapolation of existing data for nitric acid vapour. The results are represented within the accuracy of the calculations by the equation:

$$\log_{10}p = -4109/T + 8{\cdot}502 \quad \text{where } T \text{ is in °K.}^{130}$$

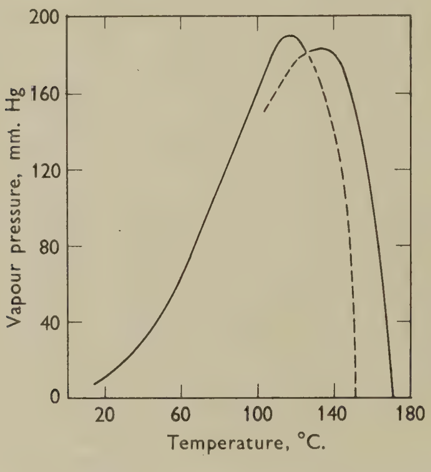

FIG. 3.—Vapour pressure above saturated aqueous solutions of ammonium nitrate

The sublimation pressure at different temperatures has been given in the form of a nomogram[131]; this, however, appears to give exceptionally high values for the vapour pressures, and the values probably include pressure due to decomposition products.

SOLUTIONS OF AMMONIUM NITRATE

Solutions of the salt in water lower the vapour pressure. The vapour pressure of aqueous solutions of the salt of various concentrations at 0°C. has been measured[132]; it is close to, though slightly lower than, the theoretical value. The vapour pressure of a saturated solution of ammonium nitrate has been measured at 2° intervals by Dingemans[84] (see Fig. 3): these results show good general agreement with those of Jänecke,[133] but because of the small temperature intervals used, two maxima in the plot of vapour pressure *vs.* temperature are evident. They occur at 117° and 132°C. where the pressures are 190·6 and 186·5 mm., respectively. The explanation offered for the two maxima is based on the existence of the crystalline modifications of ammonium nitrate. The cusp between the two curves coincides with the transition temperature between the solid phase I and solid phase II, and is at 125°. There are more recent determinations of the vapour pressure of aqueous ammonium nitrate solutions.[134, 135] The values are in agreement with those found earlier. Further data are available.[49, 136–138] The vapour pressure of a solution saturated with both lead and ammonium nitrates showed a maximum at 102·1° of 114·4 mm.[139] When the vapour pressure curve is plotted relative to that of water it consists of three sections, each nearly straight, with abrupt changes of slope at 84·2° and 125·2°, both corresponding to transition points of solid ammonium nitrate. The vapour pressure curves show that the ammonium ion is only very feebly hydrated.[135, 158]

The vapour pressure of both ammonia and nitric acid over aqueous ammonium nitrate solution has been found for concentrations from 55 to 85 wt.-% of the salt.[140] The vapour pressure due to ammonia is considerably greater than that due to nitric acid; hence in the preparation of the salt from these substances it is advisable to maintain an acid solution to avoid loss of ammonia. Total vapour pressure curves for the system ammonia–ammonium nitrate–water have been given.[63] The vapour pressure increases rapidly with increasing ammonia concentration. The vapour pressure over a solution of ammonium nitrate and ammonium carbonate has been determined.[141]

Supersaturated solutions of the salt do not show any abrupt change in vapour pressure–temperature curves as the supersaturated region is approached.[142]

Vapour pressures have been measured also for some aqueous solutions saturated with respect to ammonium nitrate and a second component. The other salts were ammonium nitrate–silver nitrate double salt,[143] lead nitrate[143] and sodium nitrate.[144] The vapour pressure of the saturated ammonium nitrate–sodium nitrate solution can be expressed from 10° to 121·1° by the equation:

$$p/p_w = 0{\cdot}6205 - 0{\cdot}004894t - 0{\cdot}0000035t^2$$

where p is the vapour pressure of the system and p_w the vapour pressure of water at temperature t.[144] The results confirm the equation

$$1/T_m = 1/T_c + 0{\cdot}00021$$

given earlier,[143] where T_m is the temperature in °K. for the maximum vapour pressure of the saturated aqueous solution of the two salts, and T_c is the eutectic temperature for a mixture of the two salts. A maximum in the vapour pressure plot was observed at 94° at a pressure of 84·2 mm. By extrapolation a temperature of 117° was found for the metastable eutectic; by direct analysis of the sodium nitrate–ammonium nitrate system the eutectic was found at 121·1 ± 0·1° at a composition of 78·2 wt.-% of ammonium nitrate.[144]

The vapour pressure lowering by solutions of ammonium nitrate in liquid ammonia at 15° is given as 26 mm. for a 0·253 molal solution, 65 for 0·745 and 208 mm. for 2·233 molal solution.[61] The vapour pressure of liquid ammonia at this temperature is 5462·5 mm.[61] The vapour pressures of solutions of the salt in ammonia were earlier determined by the same investigators at 10° [146, 239] and by others at 25°.[147, 148]

BOILING POINT OF SOLUTIONS

The boiling points of aqueous ammonium nitrate solutions have been recently determined over a wide concentration range[56] and some of the results are shown in Table VI. This study is more comprehensive than that of Gerlach (Mellor, II, 837), but does not extend to such high concentrations.

Table VI.—Boiling Point of Aqueous Ammonium Nitrate Solutions[56]

Concentration of ammonium nitrate		Boiling point, °C.
Wt.-%	Molality	
10·51	1·47	102·0
20·09	3·14	103·0
28·72	5·03	104·9
43·10	9·46	108·5
50·66	12·83	111·0
61·87	20·27	116·5
68·78	27·52	120·9
80·32	50·99	129·6
87·40	86·65	145·7

Thermodynamic Properties

The standard free energy of formation of ammonium nitrate has recently been independently calculated as −43·82 kcal./mole[129] and as −43·86 kcal./mole,[149] values showing excellent agreement. When calculated from the data for the free energy of solution and the free energy of formation of the ammonium and nitrate ions, a value of −43·96 kcal./mole was obtained for the free energy of formation of this salt.[149] The entropy of the salt was also calculated by the same investigators again in close agreement. The results were 36·0 for the entropy at 25° [129]; 36·11 ± 0·05 for the entropy of phase IV at 25° (298·16°K.) and 39·31 ± 0·05 for the entropy of phase III at 41·8° (315°K.),[149] all expressed in g.-cal. per mole per °C. The entropy was also calculated from existing data and this, too, gave 36·0 for the entropy at 25°.[129]

The enthalpy of the molten salt has been calculated at temperatures up to 269°.[129] The extrapolated value is 8·15 kcal./mole at the melting point 169·6°C., based on solid at 25°. These data together with the dissociation pressure were used to calculate the heats of dissociation, ΔH, for the reaction

$$\underset{\text{liquid}}{NH_4NO_3} \rightleftharpoons \underset{\text{gas}}{NH_3} + \underset{\text{gas}}{HNO_3}$$

Temperature, °C.	169·6	200	250	300	350
ΔH, kcal.	39·33	38·92	38·25	37·65	37·12

At the three highest temperatures extrapolated values had to be used for the enthalpy of nitric acid, but the results are comparable with 39·8 kcal./mole, average heat of vaporization found for the salt from 169·6° to 350°. The standard heat of formation of the salt has been estimated as −87·3 kcal./mole.[131] The heat of combustion of ammonium nitrate at constant volume was calculated to be 50·3 kcal./mole.[150]

A latent heat of sublimation of the salt of 41·8 kcal./mole is given.[131]

SPECIFIC HEAT

The specific heat of the salt has been measured over a very wide range of temperature. When followed from −258° to 42°C., only two anomalies were found at −17·1° (mean) and at 32·1°C.[149] When the specific heat had been measured previously from −90° to 10°C. an anomaly at −60·4° was reported,[115] but this point was not observed in the measurement over the wider range. Some of these values for the specific heat are given in Table VII.

Table VII.—Specific Heat of Ammonium Nitrate[149]

Temperature, °C.	Specific heat, g.-cal./mole/degree	Temperature, °C.	Specific heat, g.-cal./mole/degree
−258·1	0·43	−56·5	27·0
−250·1	1·51	−34·6	29·35
−209·0	9·24	−18·9	31·13
−170·4	14·65	−12·9	30·03
−128·9	19·23	10·1	32·21
−87·6	23·68	29·6	33·65
−62·8	26·34	35·7	28·93
−58·7	26·65		

The figures show the change in specific heat as the phase changes occur. The specific heat drops by 5·3 g.-cal./mole/°C. as the transition from phase IV to phase III occurs; this decrease is attributed to the complete rotation of the ammonium ion in phase III, in contrast to fully excited torsional oscillation in the phase IV state.[149] The mean specific heat for phase I, estimated from the enthalpy figure, is 45·6 g.-cal./mole/degree, but because of its derivation it cannot be regarded as highly accurate.[129]

For the molten salt, the heat capacity estimated from the slope of the enthalpy–temperature graph is 38·5 g.-cal./mole/degree.[129]

LATENT HEAT OF FUSION

The latent heat of fusion of the salt was found to be 1·10 kcal./mole,[86] but a newer and probably more reliable estimate is 1·53 kcal./mole.[87] From vapour pressure data the latent heat of melting was calculated to be 1390 g.-cal./mole for ammonium nitrate I; for the metastable phase II the value was 2,310.[84] Values for the activation energies for some of the solid phase transitions have been calculated[105] and some of the heats of transition between the solid phases have been determined.

For the transition between forms I and II, 980 g.-cal./mole are liberated and between phases II and III 310 g.-cal./mole.[102] Later estimates for these two heats of transition, based on vapour pressure data, were from forms I to II 980 g.-cal./mole and from form II to III 358 g.-cal./mole,[104] which show satisfactory agreement. During the transformation from phase III to phase IV, 400 g.-cal./mole are liberated.[103] The heat of transition for the metastable change from phase II to phase IV at 50° is given as 160 g.-cal./mole.[96]

SPECIFIC HEAT OF AQUEOUS SOLUTIONS

The specific heats of aqueous solutions of ammonium nitrate have been determined at 25° with an accuracy estimated as ±0·008%. The method was a differential one, using twin gold calorimeters and temperature measurement with a multi-junction thermocouple.[151] A selection of values for both specific heat of the solution and apparent molal heat capacity of the salt is given in Table VIII.

Other results, though not so extensive, are in agreement.[152–154] The specific heat of the solution increases gradually with temperature; for a 1·110 molal solution the specific heats at 25°, 50° and 75° were 0·9286, 0·9310 and 0·9338, respectively.[153] The results with more concentrated solutions appear to be anomalous, but the authors suggest that this may be due to experimental error. The value for the specific heat obtained by assuming those for the individual ammonium and nitrate ions is in good agreement with that determined experimentally.[155]

The specific heats, W_c, for solutions are given within ±0·5% at 32·3°C. by the equation:

$$W_c = 0{\cdot}9985 - 0{\cdot}00765857C + 0{\cdot}000030811C^2 - 6{\cdot}473 \times 10^{-8}C^3$$

where C is the concentration of the solution in wt.-%.[156]

Table VIII.—Specific Heat of Aqueous Ammonium Nitrate and Apparent Molal Heat Capacity at 25°C.[151]

Concentration, molality	Specific heat, 25°, g.-cal./deg.	Apparent molal heat capacity
0·0	1·00000	—
0·1012	0·99211	1·5
0·1928	0·98534	2·82
0·4065	0·97044	4·96
0·8433	0·94361	8·66
1·5093	0·90907	12·52
2·4323	0·87000	16·20
3·2533	0·84157	18·667
7·5672	0·74185	25·269
12·6314	0·67681	28·590
17·4353	0·63850	30·376
23·9978	0·60481	31·945

HEAT OF SOLUTION AND DILUTION

Recent values for the heats of solution and dilution agree with those previously given (Mellor, II, 837). A calorimetric method has shown the variation of the heat of solution with temperature and also the heat of solution, L, of the last mole of salt required to give a saturated solution.[157] The agreement between experiment and calculation was always within ±2%. The quantities measured were the heat of solution in much water Q, the heat of dilution, D, of a saturated solution to the condition corresponding to Q, and the heat produced, E, by adding a sufficient quantity of water to a large volume of saturated solution such that it would dissolve one further mole of salt at saturation. These quantities are related by the equation:

$$L' = Q - D - E$$

where L' is the calculated heat of solution. The following values were obtained for ammonium nitrate at 0° and 19° respectively: Q, $-6{\cdot}48$, $-6{\cdot}2$; D, $-2{\cdot}7$, $-2{\cdot}5$; E, $-0{\cdot}79$, $-0{\cdot}65$; L', $-2{\cdot}99$, $-3{\cdot}05$; whilst the experimental values for L were $-3{\cdot}04$ and $-3{\cdot}06$.

Other values for the heats of solution and of dilution have been given.[25, 132, 159] A temperature coefficient for the heat of dilution has been calculated from the heats of dilution at different temperatures and it certainly applies at temperatures intermediate between those used.[160] The following figures illustrate the heats of dilution obtained, Q g.-cal., when a solution containing 1 mole of salt and 2·5 moles of water is diluted to contain m moles of water.[160]

Temperature	Q	m	Q	m	Q	m
18·2°C.	2462	100·4	2522	134·2	2588	201·5
25·0°C.	2278	100·3	2332	134·2	2382	201·6

The heat of dilution, at 0°, decreases as the initial concentration of the solution is reduced.[132] The values are calculated from Kirchoff's law after accurate measurement of the vapour pressure of the solutions.[132, 138] The formation of a saturated solution is accompanied by an absorption of heat which is greater than the subsequent absorption during dilution of the solution.[159]

The heat of solution of ammonium nitrate in liquid ammonia at −33·4° has been estimated by measuring the amount of ammonia evaporated during solvation of the salt. The heat of solution is positive, like that of most salts in this solvent; the value given is 5700 g.-cal./mole, for a solution containing 3·5 wt.-% of salt.[161] A value of 6·75 kcal. has been more recently given for the molar integral heat of solution of the salt in liquid ammonia also at −33·4°.[162]

CRYOSCOPIC EFFECT AND ACTIVITY COEFFICIENTS

The cryoscopic effect of ammonium nitrate in aqueous solution has been reported[163, 164]: in the former study dilute solutions only were used and the results are presented in the form of the Lewis and Randall function j. There is evidence of a factor which, in the results it produces, is similar to association. It has been suggested that it is possibly the consequence of an undissociated molecule of the salt and a nitrate ion combining together,[164] but, in fact, the same effect is observed in varying degrees with other ammonium salts,[163] though it is negligible with other uni-univalent salts. The cryoscopic effect of ammonium nitrate in anhydrous acetic acid has been determined from the freezing point depression.[165, 166] The salt behaves as if it were associated into at least binary ion pairs.[166]

Table IX.—Activity Coefficient γ for Aqueous Ammonium Nitrate at 25°C.

Concentration molality, m	Activity coefficient, γ	m	γ
0·1	0·740	4·0	0·331
0·2	0·677	6·0	0·279
0·5	0·582	8·0	0·245
1·0	0·504	10·0	0·220
2·0	0·419		

The osmotic and activity coefficients of aqueous solutions have been carefully measured by the isopiestic vapour-pressure method,[167] reproducibility being about ±0·05% for duplicate determinations. These values for the activity coefficients, given in Table IX, are slightly lower than those of Redlich and Rosenfeld,[168] which were derived from freezing point data extrapolated to 25°. The activity values for the nitrate are much lower than those for the halides.[167] The authors attribute this to ion-pair formation, which is thermodynamically equivalent to incomplete dissociation.

The activity coefficients for ammonium nitrate in liquid ammonia have been determined at −50° for solutions up to 1·0 N.[169] The results differ considerably from those calculated and from earlier determinations. Even on using the Debye–Hückel equation agreement between experimental and calculated values is satisfactory only between 0·002 and 0·2 N. Some values obtained are 0·953 at 0·0001, 0·824 at 0·001, 0·466 at 0·01, 0·216 at 0·1 and 0·104 at 1 N. Hunt[147] has estimated the activity coefficients in ammonia solutions from vapour pressure data at 25°, and found them to be very low. He found also that the solutions deviated from Raoult's law in both the concentrated and dilute regions.

Apparent Molar Volume

The apparent molar volume of the salt in both water and ammonia solutions increases with increasing concentration of the solute.[170] This change is much greater with ammoniacal solutions than it is with aqueous solutions of the same concentrations, and the actual values for the molar volume of the salt in water are much greater than are those in ammonia and greater also than the molecular volume of the salt itself. Geffcken and Price have measured the molecular volume in water with solutions up to 1·5 N.[171]; the relationship with the concentration, c, was: $\phi = \phi_0 + k\sqrt{c}$ where ϕ_0 is the value at infinite dilution, 47·00. The constant, k, has the value 1·06.

Kruis[172] has also made some measurements of the apparent molar volume by means of a dilatometer: he found that when this quantity was plotted against the square root of concentration it gave a slightly sigmoid curve.

Table X.—Apparent Molar Volumes of Ammonium Nitrate in Water and Ammonia

Solutions in ammonia at 15°C.[170]		Solutions in water at 20°C.[170]		Solutions in water at 35°C.[55]	
Wt.-% of salt	ϕ c.c.	Wt.-% of salt	ϕ c.c.	Wt.-% of salt	ϕ ml.
0·65	7·49	0·93	47·6	7·9779	49·6 ±0·1
1·42	16·94	1·92	47·9	14·533	49·9 ±0·1
2·87	23·06	2·97	48·26	18·352	49·9 ±0·1
4·54	26·12	4·10	48·6	28·572	50·27±0·05
5·52	27·69	6·64	48·93	38·071	50·60±0·04
—	—	10·81	49·75	50·378	51·05±0·03
—	—	15·54	50·24	59·457	51·38±0·02
100	46·27	18·36	50·46	66·012	51·57±0·02

The most recently determined data are the values for aqueous solutions at 35°C. given in Table X.[55] The authors give the probable accuracy, which is dependent on the accuracy of measurement for the density of the solutions concerned.

The apparent molar volume in methanol solution also increases with increasing concentration.[33] The values are given in Table XI.

Table XI.—Apparent Molar Volume of Ammonium Nitrate in Methanol and Density of the Solutions at 25°C.

Concentration, molarity	Density	ϕ ml.
0·2518	0·7996	36·40
0·4679	0·8101	37·99
0·7763	0·8247	39·47
0·9080	0·8308	39·89

Magnetic Susceptibility and Anisotropy

The magnetic anisotropy of the salt has been followed as a function of temperature.[173, 174] It decreases stepwise at 32°, 84° and 125° where phase transitions occur and is zero above 125°.[173] This is in accordance with *X*-ray data on the structure. Above this temperature the nitrate ion possesses spherical symmetry. Values for the diamagnetic susceptibility have been given as $-33{\cdot}05 \times 10^{-6}$ e.s.u.,[175] and $-0{\cdot}343 \times 10^{-6}$ c.g.s.[176] For both paramagnetic and diamagnetic anisotropy[177] the influence of the crystal structure on the intrinsic anisotropy of the nitrate group is considered. The magnetic susceptibility of ammonium nitrate at the phase transition temperatures is so small that it can be due only to the changed arrangement and not to changes in the electron states.[178] In another study,[192] the relationship between molar susceptibility and coordination number for ammonium salts was investigated.

Hydrolysis and pH Values of Aqueous Solutions

The pH values of dilute solutions of ammonium nitrate approach 7 but are always slightly acid. As the solution changes from 0·1 N. to 0·01N. to 0·001 N. the pH changes from 5·43 to 5·89 to 6·45 at 15°.[179] Other measurements have been made.[180, 181] The pH values of ammonium nitrate and chloride solutions were almost identical, and the average value for the hydrolytic constants of these salts was $1{\cdot}4 \times 10^{-10}$.[181]

By using tritium as a tracer, a half-time reaction period of about 3 minutes was found for the exchange of hydrogen between ammonium nitrate and 54% nitric acid.[182] Previously the exchange between NH_4^+ and D_2O has been shown to be very slow. At 0° after 10 minutes exchange had occurred to 82%, but when the solution contained an excess of nitric acid the degree of exchange was only 58% after the same time.[183] The exchange which does occur is a result of the reaction $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$, producing some rapidly exchanging ammonia. The presence of acid suppresses this reaction and so reduces the amount of hydrolysis and exchange, but not to the same degree since the production of free ammonia is affected. This is in accordance with earlier observations.[181]

Electrical Conductivity

The electrical conductivity of solid ammonium nitrate as measured on a Wien-type bridge was found to increase exponentially with temperature and showed two transition points at 82° and 125°. On cooling the lower transition point showed considerable hysteresis and occurred at about 70°.[184] However, the transition points in this case are close enough to the phase transition temperatures to imply that the change in electrical conductivity corresponds with the change in crystal structure.

The electrical conductivity of aqueous solutions of the salt has been determined by Campbell and Kartzmark with an accuracy of ±0·002% over a wide range of concentrations at 25°,[185] 35°,[55] 95° [58] and at 180°.[186] Stokes' values at 25° [187] show excellent agreement with those of Campbell and Kartzmark. The conductivity of ammonium nitrate solutions at 100° has been measured.[81] Another recent study has used temperatures of 25°, 75° and 125°.[188] Other results are available at 25°.[189] A few of the results obtained by Campbell and Kartzmark are given in Table XII. They appear to be slightly higher than the earlier values (Mellor, II, 838); the equivalent conductivity at infinite dilution at 25° is 144·84.[187]

From more recent measurements of the conductivity of dilute solutions at 35° the limiting equivalent conductivity is calculated to be 174·21 mhos, after making corrections for the hydrolysis of the salt based on the known hydrolysis constant of the ammonium ion.[190]

Table XII.—Electrical Conductivity of Aqueous Ammonium Nitrate

Temperature, °C.	Concentration		Density, g./ml.	Specific conductivity, mhos cm.$^{-1}$	Equivalent conductivity
	Wt.-%	Molarity			
25	0·80	0·100	1·001	0·1227	112·95
	7·81	1·004	1·029	0·1017	101·32
	28·74	4·020	1·120	0·3085	76·78
	41·01	6·036	1·178	0·3809	63·12
	46·54	7·015	1·206	0·3979	56·73
	51·98	8·011	1·234	0·4036	50·36
	57·31	9·043	1·262	0·3973	43·93
	68·49	11·282	1·319	0·3538	31·3
35	0·4324	0·0538	0·9958	0·00823	153·1
	7·9779	1·0234	1·0269	0·1222	119·4
	28·572	3·9749	1·1136	0·3545	89·17
	50·378	7·6705	1·2188	0·4590	59·84
	66·012	10·749	1·3055	0·4141	38·52
95	1·605	0·1940	0·9677	0·0534	275·3
	19·895	2·576	1·0365	0·4781	185·6
	53·12	7·95	1·198	0·7776	97·81
	69·54	11·13	1·281	0·6898	61·99
	85·58	14·81	1·385	0·4252	28·71
180	8·5160	0·9868	0·9276	0·3752	380·2
	54·907	7·854	1·145	1·122	142·9
	78·84	12·70	1·290	0·8828	69·51
	100·00	18·0	1·44	0·433	24·1

The specific conductivity of the solution shows a maximum at a concentration of about 50 wt.-% of the salt at 25°, whilst at 180°C. the maximum has shifted to approximately 70 wt.-%.

All attempts to correct the conductance for the viscosity of the solution result in over-correction, so that the equivalent conductivity appears to increase with concentration.[57, 81] This observation indicates that viscosity changes are not the only changes affecting conductivity; this has since been confirmed,[188] and similar effects were shown to occur in the ammonium nitrate–acetamide system by the same authors.[191] Similarly the change in fluidity of the solution could not be made to account for the increase in conductivity at higher temperatures, and at higher concentrations.[58] It is worth noting[57] that ammonium nitrate solutions show remarkable agreement with the Walden modification of the Ostwald formula (Partington, V, 347). A semi-empirical equation derived from the Debye–Hückel–Onsager limiting law was said to be successful in calculating the conductivity of concentrated solutions of ammonium nitrate.[193] An earlier extension of this law allows the conductivity to be calculated in good agreement with practical measurements, for dilute solutions, up to 5 M.[187, 194]

When the change in conductivity of an aqueous solution is followed as a function of temperature from 5° to 60°, two breaks occur at 25° and 29·5°.[195] Between 95° and 180° the temperature coefficient of the electrical conductivity drops continuously as the concentration rises from 1 to 10 molar.[186] It has a value of 0·00743 at 1 M., 0·00584 at 5 M. and 0·00509 at 10 M.[186]

The conductivity data suggest marked ion-pair formation; its extent has been estimated.[187] Diffusion coefficients vary from 1·79 to $1{\cdot}34 \times 10^{-5}$ cm.^{2}/sec. for diffusion columns whose mean concentration changes from 0·05 to 7·6 M.[187] These experimental values agree to within 2% (up to 6 M.) with the theoretical figures, when allowance is made for the degree of dissociation found by conductivity measurements. When the theoretical expression for conductivity was tested,[194] considerable deviations from experimental values were found. This was attributed to ion-pair formation. There is an earlier estimate of the degree of association based on conductivity and osmotic pressure measurements,[196] whilst other earlier workers concluded, from the similarity of conductivity, that if alkali halides were completely dissociated then so must be ammonium nitrate.[197]

Some measurements have been reported of the conductance in methanol and ethanol solutions of ammonium nitrate.[198] The conductivity of dilute ethanol solutions at 25° was measured and showed considerable deviations from theoretical data (ionic mobilities were calculated).[145]

The conductivity of solutions of ammonium nitrate in anhydrous hydrogen cyanide at 18° was determined[39]; in this solvent the experimental results showed good agreement with the Debye–Hückel–Onsager equation. The conductivity of ammonium nitrate–acetamide mixtures has been measured.[191]

From measurements of the electrical conductivity of solutions of ammonium nitrate in liquid ammonia at −40°, a dissociation constant of $4{\cdot}3 \times 10^{-3}$ was obtained.[199] The sum of the atomic radii was 5·18 A.[199]

Electrochemical Properties

Electrocapillarity in aqueous ammonium nitrate has been investigated in (i) 1·0 M., (ii) 0·2 M., (iii) 0·02 M. solutions, all of which were 0·002 M. with respect to mercuric nitrate and nitric acid.[200] The positions of the maximum in each curve were measured at 25°, 50° and 75° and were at (i) 0·887, 0·862, 0·846, (ii) 0·933, 0·921, 0·914 and (iii) 0·961, 0·961 and 0·953 volts, respectively. The maxima occur at lower voltages at higher temperatures, a result which can be accounted for, in part at least, by a reduced tendency for adsorption to occur and an increased tendency towards random distribution of the solvent dipoles at higher temperatures. Electrocapillarity curves have been determined for the salt in methanol and in aqueous ethanol solutions.[201, 202] The decomposition potentials of ammonium nitrate determined in ammonia and water solutions are 1·34 and 2·04 v., respectively. The decomposition potential is lower in ammonia than in water, which is usual with ammonium salts.[203]

Studies of electro-endosmosis in ammonium nitrate solutions have been reported.[204, 205] From the measurements zeta potentials, which are independent of the capillary radius for a limited range, are calculated for a wide range of solution concentrations.

Liquid junction potentials in cells of the calomel type show an average potential difference of 2·61 mv. for a salt bridge of 10 M. aqueous ammonium nitrate at 35°.[185] The potential difference across the phase boundary between solutions in equilibrium in water and in amyl alcohol, 5·3 mv., also in a calomel cell, shows that the amyl alcohol solution is positive with respect to the aqueous solution.[206]

The electrode potentials of 0·1 N. ammonium nitrate solutions in water–ammonia mixtures at 20° are as follows:

Concentration of ammonia, N.	0	4·002	7·951	16·04	20·10
Electrode potential, v.	0·5232	0·4741	0·430	0·3757	0·3542

They show steady decrease as the ammonia concentration increases. By extrapolation a value of 0·30 v. is found in pure ammonia.[207]

The capacity of the electrical double layer between mercury and solutions of ammonium nitrate in methanol at 25° is similar to that measured with water at higher temperatures.[208]

Divers' liquid has been used as solvent in polarographic studies.[209]

Miscellaneous Properties

The coefficient of cubic expansion of solid ammonium nitrate has been measured by the dilatometric method from −72·2° to −40·2° [116]; no abnormalities were shown in this experiment to indicate a phase transition, but the establishment of equilibrium was very slow. The same method has been used to follow the phase transformations.[210] The mean coefficient of cubic expansion for aqueous solutions of the salt, between 25° and 78° is $5{\cdot}3 \times 10^{-4}$ (accuracy ±3%) over the range of concentrations from 3 to 16 molal, but slightly smaller at concentrations outside this range.[211] The author suggests that the constancy of the expansion coefficient may be due to a lattice structure of solute existing in the solution. The coefficient for the thermal expansion of molten ammonium nitrate was found to be $4{\cdot}3 \times 10^{-4}$.[54] The relative viscosity of the molten salt at 180° is 10·1,[78] and the activation energy for viscous flow is 4·6 kcal./mole.[212] The viscosity of mixtures with other nitrates was measured in addition to that of the pure salt.[212] By zone-melting ammonium nitrate some cation impurities may be rejected.[213]

The thermal conductivity of ammonium nitrate has been determined.[154] The mean coefficient of thermal conductivity from 0–100° was 0·205 kcal./mole/hr./°C. with a variation not exceeding 5–6% in this interval. The specific gravity varied from 0·68 to 0·76; hence a considerable volume of air must have been trapped within the material.

The coefficient of friction between clean dry crystals of ammonium nitrate, measured by the damping effect on a pendulum, is 0·50 ± 0·05.[214]

The surface tension of aqueous ammonium nitrate has been determined over a range of concentrations at elevated temperatures.[215] The results at 100° are given in Table XIII; the value 103·8 for the molten salt is that obtained by extrapolation.

The surface tension of 0·3 N.-ammonium nitrate in aqueous ethanol mixtures at 23° [216] falls rapidly with increasing ethanol concentration (wt.-%), as follows, 0%, 73·0; 10%, 50·6; 25%, 37·0; 50%, 29·1; 75%, 25·3; 95%, 22·8; and at 100%, 22·5 dynes per cm. The surface tension has also been measured for the ammonium nitrate–silver nitrate double salt.[215]

Table XIII.—Surface Tension of Aqueous Ammonium Nitrate Solutions at 100°*C.*

Wt.-% of salt	σ, dynes/cm.	Wt.-% of salt	σ, dynes/cm.
100	103·8	30	63·3
88	85·5	20	61·6
54	68·5	10	60·1
50	67·5	5	59·2
40	65·3	0	58·7

The Faraday effect, the magnetic rotation of plane polarized ultra-violet light, produced by aqueous ammonium nitrate solution is practically independent of its concentration.[217–219] The corrected molecular rotation of ammonium nitrate increases with increasing concentration.[217] The salt did not produce any detectable effect on radiation of microwave frequencies of about 3 cm. wave-length.[220] The Raman spectrum of the salt has been studied.[21]

The light scattered by aqueous ammonium nitrate solutions is depolarized,[221] owing largely to the anisotropic nature of the nitrate ion.

The refraction and dispersion properties of solid ammonium nitrate[222–224] and of aqueous solutions have been reported,[171, 172, 225, 226] and selected data are given in Table XIV. The molar refraction has been reported for alcoholic solutions.[223] From the refractive index of dilute solutions, the equivalent refraction and dispersion were calculated and their dependence on concentration shown for dilute solutions,[171, 172, 226] and for solutions up to saturation at 25°.[225] The equivalent refraction shows a slight decrease with increasing concentration of the solution.[171, 225] The extrapolated value of 15·31 at infinite dilution agrees well with that obtained by calculation, 15·33. The relationship of the specific refraction to the osmotic pressure has been shown,[224] it being assumed that the osmotic pressure is proportional to the concentration and that the gas laws hold in dilute solutions.

Table XIV.—Refractive Index, Molecular Refraction and Apparent Molar Volume of Aqueous Ammonium Nitrate at 25°[225]

Concentration normality	Density of solution	Apparent molar volume	Refractive index $n_{D_3}{}^{25}$	Molar equivalent refraction R_{D_3}
0	0·99707	—	1·33254	(15·31)
1·1555	1·03353	48·635	1·34350	15·292
2·0506	1·06100	49·014	1·35172	15·282
3·6944	1·11025	49·558	1·36637	15·258
5·9211	1·17483	50·174	1·38540	15·226
7·4567	1·21819	50·542	1·39810	15·207

The refractive index of solutions of the salt in aqueous ethanol has been measured at 15°, 20° and 25°.[227] The temperature at which a solution shows maximum refractivity is lowered as the concentration of ammonium nitrate increases[228]; however, no direct relationship between these two factors could be established. The magnetic double refraction of an aqueous solution of ammonium nitrate (54 g. in 100 c.c.) was found to be +0·14.[229] Ammonium nitrate is said to show triboluminescence.[230]

The absorption of supersonic waves by aqueous solutions of the salt has been measured for a range of temperatures and concentrations and found to be greater than that predicted by theory.[231]

The nuclear magnetic resonance spectra of neutral solutions of ammonium nitrate show a single proton resonance peak, but slightly acid conditions bring out the ammonium spin-spin triplet.[232] Proton resonance has been studied as a function of concentration; at all concentrations there was a single resonance peak.[233]

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CHEMICAL PROPERTIES OF AMMONIUM NITRATE

THERMAL DECOMPOSITION AND EXPLOSIVE SUSCEPTIBILITY

When heated, ammonium nitrate decomposes in several ways; Berthelot (Mellor, II, 840) gave seven different reactions which may occur. Thermal dissociation to form ammonia and nitric acid and decomposition into nitrous oxide and water are the commonest effects, but it appears that all the other reactions may take place to varying degrees according to the conditions. The mode of decomposition is particularly affected by the temperature and its rate of increase.

Much study by numerous workers has been devoted to the decomposition, but unfortunately there are many intractable factors, which make comparison of the results of different investigators doubtful and difficult. Since generally a number of reactions appear to take place simultaneously, and since it is difficult to estimate the contribution of each, the field becomes confusing. However, one recent study has succeeded in measuring the thermal dissociation pressure independently for the decomposition (see page 524), but it must be remembered that dissociation always occurs during chemical decomposition; hence ammonia and nitric acid will always be present in the vapour phase. Another feature is that, as nitric acid is the more soluble in the molten salt, the melt tends to become acidic.

Thermal decomposition appears to begin at about 170° [1–3] or 180° [4] but in the presence of catalysts it can be appreciable at about 150°; at these temperatures the main reaction is:

$$NH_4NO_3(l) \rightarrow N_2O(g) + 2H_2O(g)$$

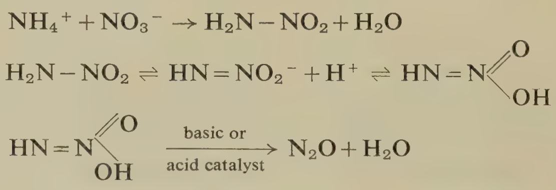
The heat of this reaction, ΔH, was given as $-16{\cdot}4$ kcal./mole at 290°,[5] and later the same authors[6] gave $-13{\cdot}21$ at 169·6°, $-13{\cdot}53$ at 200°, $-14{\cdot}03$ at 250° and $-14{\cdot}58$ kcal. at 300°. The activation energy is 31·4 kcal./mole.[1] A thermo-gravimetric study of the thermal decomposition recently gave 36·5 kcal./mole for the activation energy.[7] An earlier value for the activation energy is $40{\cdot}5 \pm 2{\cdot}5$ kcal./mole.[8] The results of the kinetic investigation suggest that the reaction is autocatalytic and occurs in the liquid phase; its rate is proportional to the product of the mass of salt and the acid concentration.[1] The initial rate is proportional to the acid concentration.[1] Thermal dissociation leads to increase in the acidity of the liquid as the ammonia formed is more volatile than the nitric acid which is, in addition, the more soluble in the molten salt.[4, 9] It was found that the presence of ammonia gas acted as an inhibitor and introducing it provided an effective means of controlling the reaction.[1]

The reaction is unimolecular.[8, 10] Under carefully controlled conditions at temperatures sufficiently low to avoid self-heating and thermal dissociation, ammonium nitrate appears to decompose unimolecularly over the entire decomposition range.[10] A similar conclusion was reached from the rate of decomposition, measured by a thermo-gravimetric balance, of samples ranging from 6 g. to 50 mg.[7]

Other investigators have concluded that the decomposition reaction is an intramolecular process.[11, 12] Two detailed mechanisms for the reaction have recently been proposed; both are dehydration processes involving an intermediate compound (NH_2NO_2), and they are both promoted by acid catalysis. The first mechanism,[1] derived purely from a study of the kinetics of the reaction, is:

$$H^+ + NH_4NO_3 \rightarrow (NH_2NO_2) + H_3O^+$$
$$(NH_2NO_2) \rightarrow N_2O + H_2O$$

where the initial reaction represents the slow step which is rate controlling. The alternative mechanism[13] is:



$$NH_4^+ + NO_3^- \rightarrow H_2N-NO_2 + H_2O$$
$$H_2N-NO_2 \rightleftharpoons HN{=}NO_2^- + H^+ \rightleftharpoons HN{=}N\begin{matrix}\diagup O\\ \diagdown OH\end{matrix}$$
$$HN{=}N\begin{matrix}\diagup O\\ \diagdown OH\end{matrix} \xrightarrow[\text{acid catalyst}]{\text{basic or}} N_2O + H_2O$$

and is based on a study of the decomposition of isotopically labelled ammonium nitrate, $^{15}NH_4{}^{14}NO_3$, under controlled conditions and fits the results. Decomposition took place at 180° in the presence of a trace of moisture; dry specimens could, in fact, be heated to 300° without decomposition. The labelled nitrous oxide formed was shown to be exclusively $^{15}N^{14}NO$, suggesting a dehydration mechanism. When labelled water, $H_2{}^{18}O$, was added as a catalyst there was no trace of the ^{18}O in the nitrous oxide. The structure of the nitrous oxide was shown by infra-red spectroscopy to have the ^{15}N atom in the terminal position.[14] A dehydration mechanism involving nitramide as an intermediate was first proposed over a century ago, and was later shown to accord with the facts,[15] but nitramide has never been conclusively shown to be an intermediate. Another recent kinetic investigation suggests that the rate-controlling step in the thermal decomposition reaction is the combination of ammonia and a hydrated nitronium ion to give nitramide.[241] The cryoscopic effect of water and nitric acid, and mixtures of these substances, on the melting point of ammonium nitrate suggests that the most likely species to occur in their presence is $[NO_3{\cdot}H_2O]^-$, but this does not have any obvious place in either of the mechanisms above, which are catalysed by these substances.[243]

The acid-accelerated reaction and the suggested unimolecular reaction theories appear to be contradictory, but recently published work reconciles these two views.[9] Whilst nitric acid is indeed catalytic, if its concentration quickly attains a constant value, then, although the rate-determining factor is bimolecular, the overall kinetics for almost the entire reaction would be of the first order. In fact, no trend of acid concentration with time could be found, for reaction times lying between 0·15 and 1·7 times the half life. This is in accord with the statement of Wood and Wise[1] that the initial rate of decomposition is proportional to the acid concentration, because their statement refers only to a very brief initial period before the rate falls below the theoretical rate; this drop is more pronounced where there is a high initial acid concentration.

Saunders[16] suggested an additional reaction which may occur after dissociation:

$$5NH_3 + 3HNO_3 \rightarrow 4N_2 + 9H_2O$$

This reaction is important because it would accelerate the chemical decomposition and also give nitrogen among the gaseous products. Another important point first made by Saunders is the strong catalytic effect of chloride. The formation of nitrogen from ammonia and nitric acid was also reported by Shah and Oza.[4] They studied the decomposition between 240° and 290° and found that the main products were nitrous oxide and water. Saunders also found these to be the main products from 210° to 260°, and they were reported to be the main products between 170° and 250° in a later investigation,[3] but above 250° sublimation was stated to be more rapid than decomposition. It appears that decomposition at temperatures up to 250–260° is almost exclusively by the main reaction to form nitrous oxide and water, together with a small amount of decomposition by a reaction producing nitrogen. Kretzschmar[2] included nitrogen in the products at 220°, with a little oxygen when the temperature reaches 250°, but he could not detect any other oxides of nitrogen besides nitrous oxide. In a continuous decomposition process at 270–310° the gas contains 3·2% of nitrogen, 0·05% of nitric oxide and 0·03% of nitrogen peroxide. There is also 0·7% of oxygen, but a loss occurs of about 18% of the ammonium nitrate by entrainment in the gases.[17]

Steady State Temperature

As a result of the reversible endothermic dissociation and the irreversible exothermic decomposition occurring simultaneously, a steady state temperature is reached in the decomposing mass.[5, 6] The relationship

$$P = \left[1 + \frac{3/2\Delta H_v}{Q - \Delta H_r}\right] \cdot p$$

was derived, where P is the ambient pressure, p is the dissociation pressure (both in cm. Hg), ΔH_r is the heat of the decomposition reaction and ΔH_v is the heat of dissociation into ammonia and nitric acid vapour (approximately 38 kcal./mole at 300°) and Q is the quantity of heat added to the system per mole of ammonium nitrate decomposed. The authors estimate that the effect of side reactions which give products other than nitrous oxide and water could safely be neglected. This agrees with other work,[16] in which 98% of the decomposition was attributed to the nitrous oxide forming reaction. By measurement of P and Q, p can be determined and thus the temperature reached by the melt can be calculated. For the adiabatic case, ($Q = 0$) the steady-state temperatures agreed with those predicted (see Table XV). Temperatures were also calculated for several other values of Q.

Later from kinetic considerations the following formula was proposed for determining the limiting temperature T, in °K. (between 200° and 350°C.), which is attained during the simultaneous endothermic dissociation and exothermic decomposition of ammonium nitrate,

$$\log P = \frac{-4{\cdot}71 \times 10^3}{T} + 11{\cdot}20$$

where P is the external pressure in mm. Hg. When the external pressure is raised the limiting temperature also rises[18].

Table XV.—Steady-state Temperature Reached by Decomposing Ammonium Nitrate under Adiabatic Conditions

Pressure, P (cm. Hg)	Temperature, °C.	
	Calculated	Experimental
38	266	271
76	289	292
114	304	306
152	314	315

The quantity of heat liberated, and consequently the temperature reached, are strongly affected by the presence of impurities, especially carbonaceous material; their presence causes a sharp increase in the final temperature attained.[6]

Reaction Rates

The reaction rates have been calculated by a number of workers,[4, 6–8, 16, 18] and most of them have been compared by Hainer,[18] who gives the rate constant as $1{\cdot}64 \times 10^{-3}$ per second,[6] or without allowance for dissociation increasing the apparent decomposition rate, $2{\cdot}3 \times 10^{-3}$. This is much lower than the value $12{\cdot}6 \times 10^{-3}$ given by Robertson[8] which is rather higher than that of other workers; this value does not include any correction for the effect of thermal dissociation. Hainer suggests that the true figure lies between these two values and that his value is too low owing to recondensation. As the rate of reaction is strongly affected by small amounts of impurities, especially moisture, some divergence in the values obtained in different studies is probable.

A recent investigation[19] showed that 200 mg. samples of ammonium nitrate started to lose weight at 80° and had lost 0·6% when the temperature reached the m.p.; this is in contrast to the findings of an earlier study,[20] in which no loss occurred at such low temperatures. Apparatus for determining the decomposition temperature on a micro scale has been described.[238]

Decomposition at Higher Temperatures

As the temperature is raised above 250° the other modes of decomposition become increasingly important and explosion often ensues. Which reaction predominates depends, however, largely on the conditions.

At 260° the reaction:

$$4NH_4NO_3 \rightarrow 2NH_3 + 3NO_2 + NO + N_2 + 5H_2O$$

is reported to occur rapidly if a small quantity of the salt is heated in an evacuated bulb[21]; after a short time a mist forms followed by an explosion. Saunders[16] stated that oxides of nitrogen other than nitrous oxide are evolved as the temperature approaches 300° (but at temperatures below 260° he found 2% of nitrogen). Immediately prior to explosion he found that the gases released were nitrogen peroxide, nitric oxide and nitrogen in the ratio 2:4:5, and immediately after the explosion there was 40% of nitrogen. More recently it was observed that the salt sublimes more rapidly than it undergoes decomposition above 250°; if it is in a confined space the nitric acid vapour dissociates further to nitrogen oxides, and if these are kept confined the gas mixture can be ignited at 290° but does not inflame spontaneously until 450° is reached.[3]

Another recent study[22] found that between 200° and 290° nitrogen peroxide is formed and acts as an autocatalyst.

Explosive Decomposition

The explosive sensitivity of the salt has been much investigated,[23–26] and the conclusion reached on reviewing the evidence is that, with reasonable care in handling, ammonium nitrate is not a dangerous material at normal temperatures.[23] The many practical investigations into the conditions required to cause detonation of the salt have included the effects of mixing with inert salts[27] and with explosive initiators[28] as well as the influence of temperature.[29] Other studies have measured the velocity of detonation, and the initiation of explosion by impact or friction.[31] Ammonium nitrate is found to be a good explosive to use in an inflammable medium, because the flame has only brief duration and there is little residual combustion.[32] However, although ammonium nitrate is widely used in explosives[33, 34] and has been involved in several serious explosions,[18, 35] it is not readily detonated, and indeed it is questionable whether the salt ever truly detonates or only decomposes explosively.[36] Side reactions occur which lower its effectiveness as an explosive well below the theoretical value.[36] The rate-controlling factor in the detonation of ammonium nitrate is stated to be endothermic gas dissociation.[37] The evidence of explosions of small samples of the salt is limited to temperatures above 250°, where side reactions are known to occur producing oxides of nitrogen in addition to nitrous oxide.[22, 38–40] These are known to form explosive mixtures with ammonia which will also be present if the sample is confined. If it is not confined, the salt can be dropped on to red-hot iron without exploding, although it will ignite.[3] Delsemme[39] found that at 290° explosion occurred with dry samples of the salt, whilst with moist samples there was rapid combustion at the same temperature. The gaseous decomposition products from the dry salt in the range from 240° to 290° showed the characteristic adsorption bands of ammonia and nitric oxide prior to explosion. But the gases from the moist sample of ammonium nitrate showed much higher concentration of ammonia and only very low concentration of nitric oxide.[39] As the evidence on both the small and large scales is that ammonium nitrate explodes only where there is confinement, sufficient at least to prevent the rapid escape of heat and of gaseous products[3] but not necessarily sufficient to give increased pressure, it appears probable that detonation is initiated by a gas-phase explosion which liberates sufficient energy to cause rapid and violent decomposition of the salt mass. Later experiments indicate that a limiting pressure of approximately 6 atm. is required, above which the explosive decomposition of ammonium nitrate occurs.[25] The explosive sensitivity can be increased if the salt is given a porous structure, by rapidly cooling it through the higher transition points in vacuo.[26]

Catalytic Effects in the Decomposition of Ammonium Nitrate

EFFECT OF WATER

Both the controlled thermal decomposition and the explosive decomposition of ammonium nitrate are strongly catalysed reactions. The presence of a small amount of water (about 0·5%) is essential for the decomposition into nitrous oxide and water to proceed smoothly at low temperatures[13]; for explosives the water content must be below 0·5%.[245] The water formed in the reaction is said to have an autocatalytic effect.[22] Dry specimens of the salt have been heated to higher temperatures

(300°) without decomposition.[13] At temperatures above 200° the presence of water appears to favour thermal decomposition by the main reaction and reduce the number of side reactions, and also to promote thermal dissociation.[39]

EFFECT OF CHLORIDES

Saunders[16] first detected the strong catalytic effect of the chloride ion on the thermal decomposition (1% being equivalent to a 25–30° temperature rise). As little as 0·1% has a marked effect on the decomposition, and chlorine can be detected in the evolved gases in proportion to the amount added to the salt. Saunders showed also that the gas composition varied in the presence of chlorides; there is a marked increase in nitrogen content. With chlorides there is frequently an induction period before vigorous decomposition commences.[16, 18] Towards the end of the induction period chlorine starts to be evolved in proportion to the amount of halide in the mixture,[36] and as the chloride present is decomposed the amount of chlorine is reduced.

Recently it has been found that chlorides promote a strongly exothermic reaction, producing nitrogen, which commences at lower temperatures and has an appreciable rate at 160°.[41]

The influence of ammonium halides on the thermal dissociation of ammonium nitrate has now been studied in greater detail.[42] The results show that the length of the induction period is independent of halide concentration, but it is an exponential function of $1/T$, where T is the temperature. Induction times vary from 5 min. at 250°, to 25 at 200°, and to 270 min. at 160° in the presence of ammonium chloride. The induction period is decreased by the presence of free nitric acid or chlorine gas. The termination of the induction period is always accompanied by the liberation of chlorine gas, which appears to be an essential activation step in the thermal decomposition under these conditions.

It has been suggested that chloride affects the decomposition only in acid melts,[43] but the melt always tends to become acid as a consequence of the dissociation of the salt. Nitric acid itself has been shown to accelerate the rate of decomposition,[1, 43] and the initial rate is proportional to the free acid concentration.[1]

EFFECTS OF OTHER MATERIALS

Carbonaceous materials are very effective in promoting the decomposition of ammonium nitrate, e.g. bag paper (1·5%) caused explosions at temperatures as low as 140°,[40] whilst oils and waxes gave similar results at slightly higher temperatures.[24, 44–46] With organic materials the acceleration is probably due to the large amount of heat liberated by their combustion, the salt acting as an oxidizing agent. It has been shown that the gas produced by slow reaction at 100° between ammonium nitrate and cellulose is almost entirely nitrogen and carbon dioxide.[47]

Other materials reported to have catalytic effects on the decomposition of ammonium nitrate are chromates[48, 41, 49–51] and nitrogen peroxide.[22] The effect of chromium in various forms, Cr_2O_3, $K_2Cr_2O_7$, $Cr(NO_3)_3$, is to accelerate greatly the decomposition rate (up to 150 times). Addition of potassium dichromate (5%) is equivalent to a 35° temperature rise.[51] The chromic ion is active at lower temperatures, but both Cr_2O_3 and $K_2Cr_2O_7$ are ineffective until the m.p. of ammonium nitrate is approached. The residue when chromium is present always contains chromic and chromate ions.[49, 50] Iodide and fluoride ions do not appear to affect the decomposition, as studied by differential thermal analysis, but the following substances mixed with ammonium nitrate in the same molar ratio give increasingly large differential temperature peaks: ammonium sulphate, sodium bromide, sodium chloride, ammonium chloride, ammonium dichromate.[41] Substances which have a smaller catalytic effect than chromium salts are chlorate, bromate, iodate and nitrite ions.[50]

The relative effects of some of these substances on the rate of weight-loss of ammonium nitrate maintained at 200° for 3 min. have been given.[51] The weight-losses are: for pure ammonium nitrate 0–1%; with $K_2Cr_2O_7$, $(NH_4)_2Cr_2O_7$ or CrO_3, 100%; $CuCl_2,2H_2O$, 70%; $FeCl_3,6H_2O$, 40–50%; $KClO_3$, 14%; $KBrO_3$, 8%; KIO_3, 2–9%; $KCr(SO_4)_2,12H_2O$, 3%; and with $NaNO_2$, 2–3%.

RETARDANTS

Among substances reported to have a retarding effect on the thermal decomposition are anhydrous salts such as sodium sulphate.[4] This effect may be due to the removal of free moisture as water of hydration for the added salt. Sulphates have also been reported to be without effect.[16] The thermal decomposition can be inhibited by addition of small quantities of urea (up to 1%).[52] The duration of effectiveness is proportional to the amount added. The urea prevents the melt from becoming acidic; after half an hour at 225° the pH of ammonium nitrate was about 2·1, but with melts containing 0·1–1·0% of urea the pH was about 6·6. The ammonium nitrate and urea appear to stabilize each other, but higher proportions of urea reduce the stability of the system, possibly owing to the instability of the urea itself.

Solutions of ammonium nitrate do not show any appreciable decomposition during evaporation at normal or reduced pressures.[53] A decinormal solution has been shown to decompose slowly at its boiling point if there is a suitable catalyst present.[54] Platinum or iridium black gives complete decomposition according to the reaction:

$$5NH_4NO_3 \rightarrow 4N_2 + 2HNO_3 + 9H_2O$$

after one or two hours. This reaction is the same as that previously proposed for decomposition of the solid in the presence of platinum black (Mellor, II, 840).

OTHER DECOMPOSITION REACTIONS

It has been stated that no appreciable decomposition of aqueous ammonium nitrate occurs during evaporation of a solution,[53] but a dilute solution does decompose slowly. The quantity of ammonium ion which is oxidized has been shown to be greater when the solution is exposed to sunlight than when it is kept in the dark.[55] The concentration of nitrate nitrogen is also reduced following exposure.[55] It has been found that ultra-violet light causes reduction of the nitrate ion and oxidation of the ammonium ion in solution, both ions being converted ultimately to nitrite ions.[56] Photolysis of crystalline ammonium nitrate by light from a high pressure mercury arc with formation of nitrate and oxygen showed a lower quantum yield than for most other nitrates used.[57]

Ammonium nitrate can be reduced by hydrogen in a silent electric discharge; the products detected were ammonia, ammonium nitrite and nitrogen peroxide.[58]

REACTIONS WITH METALS AND THEIR OXIDES

Fused ammonium nitrate rapidly oxidizes and dissolves many metals (Mellor, II, 841). The reaction of the molten salt with powdered metals is often violent and accompanied by evolution of white or brown fumes and sometimes results in explosion; zinc, cadmium, copper, iron, lead, aluminium, magnesium, manganese, cobalt, nickel, bismuth, chromium, tin and antimony were the metals tested.[59] In another report aluminium, manganese, iron and tin were said to be exceptional in being the only metals above hydrogen in the electropositive series not to react.[60] Another investigation put iron and aluminium among the metals not attacked, but found iron to be attacked in the presence of sulphates or chlorides.[61] These differences may be due to the metals not being sufficiently finely divided or, in the cases of aluminium, iron and tin, to a coating of oxide on the metal surface. In another investigation no exothermic reaction was detected between ammonium nitrate and iron filings or aluminium at temperatures up to 179° and 173° respectively. With copper an exothermic reaction was observed at 173°, with brass strips reaction took place at 167° and with stainless steel at 199°, but with powdered zinc rapid reaction occurred at 117°.[62] With copper the equation has been given as:

$$Cu + 3NH_4NO_3 \rightarrow Cu(NO_3)_2 + N_2 + 2NH_3 + 3H_2O$$

Bismuth gives a similar reaction.[60] With sodium a yellow explosive substance, possibly disodium nitrite, is the final product; the intermediate products are first sodium nitrate and nitrite and then sodium hyponitrite, and sodamide before the explosive material is formed.[237]

In alcoholic solutions of ammonium nitrate, cobalt readily dissolves as a bivalent ion when it is used as an anode. Under the same conditions iron is passive, but nickel dissolves at temperatures above 25° and at low current densities dissolves chemically.[63] Chromium also dissolves as a bivalent ion, but only at high current densities.[63] Cadmium dissolves rapidly in both aqueous and alcoholic solutions with or without the passage of an electric current.[64]

When copper is slowly dissolved in aqueous ammonium nitrate, as happens during corrosion, the products are copper tetrammine nitrate, $Cu(NH_3)_4(NO_3)_2$, and basic copper nitrate, $Cu(NO_3)_2,3Cu(OH)_2$.[65]

Fused ammonium nitrate dissolves several metallic oxides to form the metal nitrate and liberate ammonia and water. The following oxides are attacked: cupric, magnesium, zinc, cadmium, calcium, barium, mercuric, nickel and uranium trioxide.[60] When ammonium nitrate is fused with a rare earth oxide for a few minutes some of it dissolves. Lanthanum oxide is rather more soluble than the others, 2·4 g. dissolving in 10 g. of ammonium nitrate. Only 0·5 g. of ceric oxide is soluble under the same conditions, whilst for all the other rare earth oxides tested about 1·5 g. dissolved. Hence by a series of fractional crystallizations a sample can be enriched in lanthanum.[66] Many metal oxides are insoluble in fused ammonium nitrate, e.g. the oxides of beryllium, aluminium, chromium (Cr_2O_3), iron (Fe_2O_3 and Fe_3O_4), thorium, stannic, tantalum, niobium, vanadium (V_2O_5), molybdenum (MoO_3) and tungsten (WO_3).[60] Hafnium oxide was found, by use of a radioactive isotope technique, to be more soluble in ammonium nitrate solution than in water.[67]

Solutions of ammonium nitrate in liquid ammonia reduce some metal oxides better than does liquid ammonia itself. Chromium trioxide is partially reduced to chromic oxide, Cr_2O_3.[68, 236] Nickel oxide slowly dissolves in a solution of ammonium nitrate in liquid ammonia to form $Ni(NH_3)_6NO_3$.[68] Although cobaltic and cobaltous oxides and ferrous oxide are unreactive towards liquid ammonia, cobaltous oxide and ferrous oxide are partially dissolved in an ammonium nitrate solution in liquid ammonia at 100°, but cobaltic oxide is unattacked.[69]

FORMATION OF COMPLEX AND DOUBLE SALTS OF AMMONIUM NITRATE AND PHASE RULE STUDIES

Complexes are formed with both ammonia and nitric acid (Mellor, II, 842). Further information on the complex acid salt ammonium dihydrotrinitrate has been given. Vapour pressure measurements of solutions of ammonium nitrate in pure nitric acid[70] indicate that the anions of the solute unite with the solvent molecules to give the complex according to the equation:

$$2HNO_3 + NH_4NO_3 \rightleftharpoons (HNO_3)_2.NO_3^- + NH_4^+$$

The *X*-ray pattern of the crystalline complex has been studied[71] and a simplified picture of the structure presents it as consisting of layers containing ammonium and nitrate ions separated by layers of nitric acid molecules, two nitric acid molecules being united by hydrogen bonds to one nitrate ion. This agrees with the structure deduced for the complex in solution. It has since been reported[72] that between −60° and +50° there is only one stable addition compound, $(HNO_3)_2$–NH_4NO_3; this melts at 29·6° and forms stable eutectics with either component, but below the eutectic point, at temperatures below 12·2°, a metastable complex exists, HNO_3–NH_4NO_3.

The system ammonium nitrate–ammonia has been the subject of further investigations.[73–77] The vapour pressure curves for the system at 0°, 10° and 20° show no addition products,[73] which is in agreement with the earlier findings. Divers' liquid, (the liquid formed when ammonium nitrate absorbs ammonia) is stated to be a stable system at a total ammonia pressure of 1 atm. only up to $23{\cdot}7 \pm 0{\cdot}7°$; above this temperature it is in a metastable condition.[74] The rates of liquefaction of four of the allotropic forms of the salt on absorption of ammonia do not differ within the limits of experimental error.[74] The system ammonia–ammonium nitrate gives two liquid layers before the critical temperature is reached for evaporation of the upper, ammonia-rich, layer[77]; a similar phenomenon occurs when water is added to the system.[77] For the system ammonium nitrate–ammonia–water the partial vapour pressures of ammonia and water have been measured by thermal conductivity of the vapour phase[76]; the partial pressure of ammonia is dependent on the ratio of ammonium nitrate to water. The system has also been studied with carbon dioxide present.[75]

The high solubility and low melting point of ammonium nitrate have contributed to interest in the equilibria and reactions between this salt and several others, as has also the prospect of commercial application of equilibrium conditions to produce other salts, and especially to convert potassium chloride to potassium nitrate. These studies have been classified below according to the metallic elements introduced into the systems by the other components.

The hydrazine nitrate–ammonium nitrate system shows no evidence of compound formation; there is a eutectic at 43° with 32% of ammonium nitrate.[78]

Systems with Other Ammonium Salts

Several investigations have been made into systems containing ammonium nitrate and other ammonium salts.[79–93]

With ammonium sulphate two complex salts, $(NH_4)_2SO_4,2NH_4NO_3$ [80–83, 94] and $(NH_4)_2SO_4,3NH_4NO_3$,[82, 83] have been reported from studies on the binary salt system and on the aqueous ternary system. Results obtained with the binary system suggest that both complexes decompose at about 180°.[83] However, Jänecke *et al.*,[80] who state that only one complex salt, $(NH_4)_2SO_4,2NH_4NO_3$, exists, give a m.p. of 310°; they also made an *X*-ray analysis of the complex. There is some evidence of limited solid solution formation between ammonium sulphate and the nitrate[84]; stable solid solutions have since been reported for up to 12 mol.-% of ammonium sulphate in the mixture.[95]

An acid complex salt, NH_4HSO_4,NH_4NO_3, is formed by the action of ammonium nitrate on concentrated sulphuric acid, or from a concentrated solution of ammonium sulphate and nitrate in sulphuric acid.[79] This salt is very hygroscopic, readily soluble in water and melts at 87°.

For the ammonium chloride–ammonium nitrate system, Bowen reported that a solid solution occurs at up to 8% of ammonium chloride,[84] but a later study of the solubility relationships of the salts in an aqueous system from 0° to 50° indicates that no complex salt, solid solution or hydrate formation exists.[85] Phase diagrams[86] for the aqueous system between −20° and 30° show that there is a triple point at −22°, corresponding to the composition 27% of ammonium nitrate, 11·4% of ammonium chloride and 61·1% of water.

The ternary system ammonium nitrate–monoammonium phosphate–water proved to be a simple ternary system with no compound or solid solution formation. The ammonium nitrate has a strong salting out effect on the monoammonium phosphate. There is a eutectic at −16·8° with a composition of 41·5% of ammonium nitrate, 2% of monoammonium phosphate and 56·5% of water.[88–90] The separate vapour pressures in the system due to ammonia and water at 25° have been given.[91]

In the binary system ammonium nitrate–monoammonium phosphate the eutectic point occurs at 147° and there is evidence of solid solutions.[96] Further detailed

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studies of the equilibrium in the system NH_4^+–H^+–NO_3^-–PO_4^{3-}–H_2O at 25°[97] and at 50°[98] show no compound or solution formation.

In the aqueous ammonium nitrate–ammonium chlorate system there is continuous formation of solid solutions.[99] The system ammonium nitrate–ammonium thiocyanate has been studied both as a binary system and in aqueous solution; formation of solid solutions is shown by both diagrams.[92] In the system ammonium nitrate · ammonium sulphamate there is no evidence of compound or solution formation.[93]

Systems With Potassium Salts

For the potassium nitrate–ammonium nitrate system there are two series of solid solutions, as either salt is capable of dissolving the other to a considerable extent. In addition these salts form a complex differing in structure from both the original salts. The aqueous system was studied in great detail from −50° to 200° by Jänecke,[100] who found a total of eight invariant equilibrium systems and a new solid phase, a solid solution of ammonium nitrate in potassium nitrate, having the crystal structure of a modification of potassium nitrate normally found only at high pressures and temperatures. There is a rise in the conversion temperature between phases II and III of ammonium nitrate as potassium nitrate dissolves to give a solid solution, and a fall in the conversion temperature between phases III and IV. An unusual feature is the ease with which the solid solution is formed. If the dry salts (0·2% of water) are mixed, solution occurs at ordinary temperatures, but it is more rapid if the mixture is heated to 50°C.[101] Solution takes place most readily with phase III ammonium nitrate, the structure of which is stabilized by the dissolved potassium nitrate so that it is stable up to 110°. The lower transition point is so lowered that with 32% of potassium nitrate direct conversion between phases III and V occurs.[101]

At 25° potassium nitrate dissolves up to 13·5% of ammonium nitrate, whilst ammonium nitrate dissolves up to 35% of potassium nitrate.[87] More recently it was found that solid solutions with up to 45% of potassium nitrate are stable at ordinary temperatures with modification III ammonium nitrate, but that modification IV reached 'saturation' with about 8% of potassium nitrate; larger proportions cause a partial conversion to phase III.[101] These results are confirmed by *X*-ray investigation; the patterns show a slight widening of the spacing, as the solution forms, indicating a slight contraction of the lattice which is consistent with random distribution of potassium ions. There was no disparity in line intensities.[101]

In other measurements at 25° of the ternary system with water, no double salt was found,[102] but these results are not entirely correct,[103] as pure ammonium nitrate does not separate from solutions containing only a small amount of potassium nitrate.

Two formulae have been given for double salts, $2NH_4NO_3{,}KNO_3$ (m.p. 170°), obtained from a solidified melt,[96] and $NH_4NO_3{,}3KNO_3$ obtained from the aqueous system.[104, 105] Another report refers to a mixed crystal which separates from a solidified melt or from the ternary system with sodium nitrate.[106]

Studies have been made of the ternary systems with lead nitrate[107] and silver nitrate[108] as an additional component of the system.

The ammonium nitrate–potassium sulphate system is complicated by the equilibrium:

$$2NH_4NO_3 + K_2SO_4 \rightleftharpoons (NH_4)_2SO_4 + 2KNO_3$$

in the presence of water. This leads to the formation of solids similar to those in the ammonium nitrate–ammonium sulphate and ammonium nitrate–potassium nitrate systems. There is no evidence of any double salt of ammonium nitrate and potassium sulphate.[94, 109, 110]

With ammonium nitrate and potassium chloride double decomposition can again occur and the formation of ammonium chloride and potassium nitrate is favoured, especially at lower temperatures; hence the solid phases tend to be composed of these salts.[111, 112] The system and its equilibrium have been studied on several occasions,[111–119] in the presence of ammonia[113] and in the presence of monoammonium phosphate.[120, 121] There do not appear to be any double salts of ammonium nitrate and potassium chloride.

Systems With Sodium Salts

In contrast to the ammonium nitrate–potassium nitrate system, the ammonium nitrate–sodium nitrate system is very simple, without solid solution formation. The eutectic temperature is about 121°; values which have been given include $121{\cdot}1° \pm 0{\cdot}1$ with a mixture containing 78·2 wt.-% of ammonium nitrate,[122] 120·8° with 79·5%,[123, 124] $121{\cdot}2 \pm 0{\cdot}2°$ with $79{\cdot}0 \pm 0{\cdot}1\%$[125] and 121°.[126] A metastable eutectic is said to occur at 117° with ammonium nitrate III.[122] The ternary system ammonium nitrate–sodium nitrate–water has been studied by several workers.[105, 127–131] A complex salt, $NH_4NO_3,2NaNO_3$, is formed[105, 128]; Karnaukhov[130] gives details of the structure of this double salt and of a thermal effect between 285° and 320° which probably reflects its decomposition. These two salts with lead nitrate do not give a ternary compound.[132]

The reciprocal system ammonium nitrate–sodium chloride has been much investigated.[126, 131, 133–138] Owing to the equilibrium:

$$NH_4NO_3 + NaCl \rightleftharpoons NaNO_3 + NH_4Cl$$

in the aqueous system, there are four salts present, but no double salts or isomorphous mixtures could be found.[126] It has been suggested that the equilibrium could be employed to obtain ammonium nitrate from the other salts in the aqueous system.[133–135, 137] The effect of ammonia on this system is to increase the solubility of the ammonium salts and cause crystallization of pure sodium nitrate.[136]

In another reciprocal system, viz., that of monoammonium phosphate and sodium nitrate in water there is again no evidence of any double salts or solid solutions.[242]

Systems With Lithium and Rubidium Nitrates

No isomorphous mixtures or double salts are formed in the system ammonium nitrate–lithium nitrate[139, 140]; the eutectic temperature is 97°. No compound or solid solution occurs in the aqueous system up to 90°.[140]

On the other hand rubidium nitrate and ammonium nitrate mixtures crystallize from aqueous solution at 25° as a continuous solid solution, because of the similarity between the ionic radii of Rb^+ and NH_4^+.[105] The two nitrates have the same type of structure, and owing to the similar ionic radius of the two cations, solid solutions containing rubidium show the phase transitions at the same temperature as for pure ammonium nitrate.[141]

Systems With Silver and Copper Nitrates

With silver nitrate ammonium nitrate gives the well-defined double salt $NH_4NO_3,AgNO_3$.[142–147] The vapour pressure of the saturated solution of this double salt has been measured from room temperature to 110° [144]; its surface tension has also been determined.[148] Magnetic susceptibility measurements on aqueous solutions of the mixed nitrates indicate the existence of a second complex salt, $2NH_4NO_3,AgNO_3$, in the solution.[149]

When solid ammonium nitrate is added to a saturated solution of cupric nitrate, more of the copper nitrate dissolves, which points to complex formation.[150] Schreinemakers gives the formula $3NH_4NO_3,Cu(NO_3)_2$ for the double salt.[150] The same complex was reported from a polarographic study, in which its stability was strongly affected by the concentration of hydrogen and nitrate ions: the complex is decomposed by alkali.[151] Milbauer and Doskar[152] state that the product formed on mixing solutions of copper and ammonium nitrates is not a true double salt but is ammonium nitrate containing some copper nitrate which is occluded or entrained during the course of crystallization.

Systems With Lead Nitrate

The addition of ammonium nitrate to a saturated solution of lead nitrate causes further dissolution of the lead nitrate. This effect diminishes with increasing temperature.[153] Although no solid exists other than lead and ammonium nitrates, viscosity and conductivity measurements indicate that the increased solubility of lead nitrate is due to complex formation, probably of the type $Pb(NO_3)_4''$.[148] That no compound occurs in the solid phases has been confirmed. This work included solubility measurements at 25° [154] and vapour pressure measurements of the saturated solutions up to the eutectic temperature, 133·8°, for the binary system.[155] Diamagnetic susceptibility, viscosity, rheochor, specific conductivity, surface tension and parachor data all show three distinct breaks when examined as a function of changing salt ratios in the solution.[156, 157] These breaks correspond to the compositions $Pb(NO_3)_2,nNH_4NO_3$ where $n=1$, 2 and 4. These results were confirmed by measurements of the magnetic susceptibility of the mixed salt solutions,[149, 158] whilst compressibility variations correspond to the complexes with $n=1$ and $n=2$.[159] Values of the refraction of solutions of the mixed nitrates suggest that only the complex with $n=1$ occurs.[244]

Systems with Calcium and Barium Salts

The ammonium nitrate–calcium nitrate–water system has regions corresponding to saturated solutions of $NH_4NO_3,5Ca(NO_3)_2,10H_2O$ and $NH_4NO_3,Ca(NO_3)_2,2H_2O$ at 10°.[160] In tests on the stability and dehydration of these double hydrates, the polymorphism of ammonium nitrate was not exhibited. *X*-Ray diagrams showed the difference in structure.[20] The regions of stability of the double salts decrease with rising temperature; both salts exist at 20°, but at 30° the dihydrate is in a metastable state.[161] Other work indicates the existence, at 25°, of a decahydrate and a trihydrate, $NH_4NO_3,Ca(NO_3)_2,3H_2O$.[162] Another thermographic analysis of the system has recently been reported.[163] In studies of the system containing also the phosphate ion, regions corresponding to a trihydrate, $NH_4NO_3,Ca(NO_3)_2,3H_2O$, were found at 25°, but the dihydrate was not found.[164–166]

There is a eutectic in the binary ammonium nitrate–calcium nitrate system at 111° with 71% of ammonium nitrate.[167]

In the system ammonium nitrate–barium chloride double salts and intermediate hydrates are absent.[168] The solubility of calcium carbonate in ammonium nitrate solutions is due to the action of the hydrogen ions produced by hydrolysis of the ammonium nitrate.[169]

Systems With Thorium Nitrate

From measurements of the density and specific refraction of solutions in the system NH_4NO_3–$Th(NO_3)_4$–H_2O, there is evidence of the existence of the following compounds in solution: $4NH_4NO_3,5Th(NO_3)_4$, $NH_4NO_3,Th(NO_3)_4$, $4NH_4NO_3,5Th(NO_3)_4,25H_2O$, $NH_4NO_3,Th(NO_3)_4,8H_2O$. At 40° the two hydrates lose water and retain $11H_2O$ and $1H_2O$, respectively. Above 50° decomposition starts.[170] Later three hydrates were isolated: $4NH_4NO_3,5Th(NO_3)_4,25H_2O$, $4NH_4NO_3,5Th(NO_3)_4,9H_2O$ and $NH_4NO_3,Th(NO_3)_4,8H_2O$.[171]

Systems With Lanthanum Nitrate

The double salt $La(NO_3)_3,2NH_4NO_3,4H_2O$ crystallizes from the aqueous system of the two nitrates, for concentrations of $La(NO_3)_3$, 40–54% and of NH_4NO_3, 14–22%.[172]

REACTIONS WITH ORGANIC MATERIALS

Ammonium nitrate is a strong oxidizing agent for organic materials[44, 173, 174] and hence at high temperatures reacts violently with most organic matter. This action is suggested as a contributory cause of some of the explosions involving the salt.[24] It has been suggested that the oxidation is due to traces of nitrous acid present in the salt.[47, 175] Findlay[47] showed that cellulosic material is slowly oxidized when kept at 100° in contact with ammonium nitrate with evolution of carbon dioxide and nitrogen in the proportion 1:2, which is that expected for complete oxidation of the cellulose to carbon dioxide and water. No oxides of nitrogen or carbon monoxide were detected. Starch acted similarly and appeared to be slightly more reactive. Recent experiments have confirmed the reaction with cellulose at 100°.[176] Ammonium nitrate is a very effective oxidizing agent for coal, converting it into humic acids. On heating the coal mixed with the salt in an air stream at 150°, oxidation is as rapid as when the coal is heated alone to 350° in the air stream. It appears that in this case the salt acts largely as a catalyst for atmospheric oxidation.[174]

The explosive sensitivity of the salt mixed with organic material varies considerably with the type of organic material and the physical conditions.[176–178] The latter effect makes the findings of different workers difficult to compare as there are so many variable factors involved, such as the size of the sample, methods of heat production, of initiation and of confinement, the importance of which cannot be estimated. The most recent studies show that with paper, or bagging cellulose mixtures, explosions can be made to occur at temperatures as low as 150°, whereas with hydrocarbon materials (waxes) no explosion takes place below 270°,[176] at which temperature probably the pure salt could have been made to explode.

The reactions involved in the oxidation of organic material by ammonium nitrate are certainly complex, and it is probable that there are a number of competing reactions. During the combustion of some mixtures of charcoal with ammonium nitrate a surging or cyclic combustion occurs. The CO_2:CO ratio is about 4:1 for the fast reaction, but at the slowest point this ratio is 16:1, and is accompanied by evolution of a greater proportion of nitrogen peroxide than occurs during the fast reaction period. The duration of a cycle varies from 2 to 50 seconds according to the mixture used. The burning rate is accelerated by several substances including sulphates, carbonates and alkali nitrates, whilst chlorides are less effective and phosphoric acid decreases the burning rate.[179]

An interesting reaction is that between ammonium nitrate and paraformaldehyde in acetic anhydride to give *cyclo*trimethylenetrinitramine, which has been studied in detail.[180, 181] When paraformaldehyde and ammonium nitrate are caused to react in glacial acetic acid the product is hexamine dinitrate, which is probably a precursor of the final product formed in acetic anhydride solution.[180]

In studies on the binary system urea–ammonium nitrate there is a eutectic point at 44·7° with 53% of ammonium nitrate, but there is no evidence of compound formation.[182] In the aqueous system two series of solid solutions are found.[183] More recent viscosity and conductivity measurements of the mixed aqueous solution indicate the existence in solution of two complexes $NH_4NO_3,CO(NH_2)_2$ and $NH_4NO_3,2CO(NH_2)_2$.[184] Two ternary systems ammonium nitrate–urea–sodium nitrate[185] and also ammonium nitrate–urea–resorcinol[186] have been studied.

Ammonium nitrate and guanidine nitrate form a eutectic mixture at 127° with 74% of ammonium nitrate in the mixture.[187, 188] Ammonium nitrate forms a compound $4NH_4NO_3,PhNH_2.HCl$, m.p. 153°, with aniline hydrochloride, but no compound was detected in the system with aniline nitrate.[189] Ammonium nitrate is used to prepare guanidine salts by reaction with calcium cyanamide. Small amounts of calcium oxide present in the cyanamide react with the ammonium nitrate to give ammonia, calcium nitrate and water. The mixture will then almost completely liquefy at 100° and the reaction

$$CaNCN + 2NH_4NO_3 \rightarrow H_2NCN + Ca(NO_3)_2 + 2NH_3$$

takes place. The ammonia, retained in the mixture by the unchanged ammonium nitrate as Divers' liquid, then reacts with the cyanamide to form guanidine.[190]

CORROSION

Aqueous ammonium nitrate causes corrosion of many common constructional metals. The effect and its inhibition have been studied by many workers.[191–218, 220]

With iron and mild steels it has frequently been shown that corrosion is most rapid where the metal is under stress; it results in the appearance of intercrystalline cracks, or cracks at the point of strain, before failure occurs.[191, 193, 197–199, 207, 209, 210, 212, 213] Single crystal specimens show no signs of attack in conditions where larger samples show intercrystalline corrosion cracks after a few hours.[199] Increased loading increases the rate of attack.[209] Electrically welded seams in steel plates show higher corrosion resistance than the parent metal, but with gas-welded seams the seam is attacked first.[200] The rate of corrosion is dependent on the carbon content of the steel and its distribution within the metal[210]; the rate decreases with increasing carbon content.[206, 212] When studied as a function of temperature, corrosion of mild steel is worse at 30° than at 45° or 60°.[191] The presence of oxygen has been reported to play a predominant rôle in intercrystalline corrosion.[214] This was shown by immersing some iron wires in ammonium nitrate solution and coating others with a film of the solution.[215] Those coated only with a film were more rapidly attacked. Single crystals exhibit stronger cathodic polarization than polycrystalline samples.[214] A slight excess of nitric acid or phosphoric acid reduces the corrosion of steel evaporators for ammonium nitrate solutions.[195]

Inhibition of the corrosive action by addition of small proportions of a suitable reagent to the solution includes the addition of thiourea,[201] of thiocyanate[203, 208] or other sulphur-containing organic compounds such as thioacetic acid or ethyl mercaptan,[203] of diammonium phosphate and lead nitrate.[206] The use of an excess of aluminium to deoxidize the steel before annealing was effective.[206] Preheating of the steel reduces the stress corrosion cracking of welds.[216] Using an aluminium cathode and passing a low voltage current for a short time is said to render steel tanks passive for a considerable time.[205] Acid resistant steels are resistant also to ammonium nitrate[202]; the amount of corrosion of stainless steels has been measured.[211]

Brass is attacked similarly to steels, cracks appearing at the points of strain.[192] The corrosive attack on copper,[196] on zinc,[217] and on aluminium[194] has also been investigated. Copper powder is attacked when exposed to the atmosphere above ammonium nitrate solutions, although it is not in contact with the liquid.[218] Solutions of ammonium nitrate in liquid ammonia strongly corrode iron and completely dissolve zinc; lead and tin are only slightly attacked by such solutions and aluminium is quite resistant.[204] Aluminium and some Cr–Ni stainless steels are resistant to aqueous ammonium nitrate solutions containing ammonia.[220]

ANALYTICAL EXAMINATION OF AMMONIUM NITRATE

Because the moisture content of ammonium nitrate has a very strong effect on the solidifying point of the salt and because the last traces of water are very difficult to remove, a simple and rapid method of moisture determination for production control has frequently been sought. The application of the Karl Fischer method has been discussed.[221] By this method moisture can be determined with an accuracy of $\pm 0{\cdot}05\%$ for values up to 1%.[239]

A suggested method for rapidly determining the moisture content of very highly concentrated ammonium nitrate solutions is based on their boiling points. A table of the concentration of melts which depends on both temperature and pressure was constructed, and gives a mean deviation of 0·1% on the moisture content, when compared with the results obtained on drying to constant weight.[222]

Use has been made of a thermistor bridge to determine the water content of the solid.[223] A stream of dry nitrogen is passed over the ammonium nitrate sample and then into a calcium hydride reaction vessel containing the thermistor. The maximum deviation of the resistance of the thermistor bridge is directly related to the water content of the sample. Known samples were used for calibration and checked by the Karl Fischer method.

The change in dielectric constant gives results with an accuracy of about 0·3% on the moist salt.[224] The moisture can also be determined by a continuous weighing method at 119°. The decomposition of the salt at this temperature proceeds at a linear rate over a very long period, while the free moisture is lost over a very short period. By extrapolation the percentage of water originally present can be determined.[225]

Double decomposition of the salt with formaldehyde has been applied as an analytical method for determining ammonium nitrate content. The method gives consistently low results which are corrected by a Kjeldahl determination on a representative sample.[226] Use can be made of the solubility of the salt in pyridine to determine the quantity of ammonium nitrate in a mixture of salts.[240]

Oil contamination of ammonium nitrate is undesirable and a luminescence method for estimating the contamination is reported to give satisfactory results.[227]

NUCLEAR CHEMISTRY

Irradiation of an ammonium nitrate solution by slow neutrons causes a (n, p) reaction $^{14}N \rightarrow {}^{14}C$ to take place. The resulting $^{14}CO_2$ can be separated from the solution with an efficiency of 99%.[228] The distribution of ^{13}N formed when ammonium nitrate is exposed to neutron bombardment and undergoes a (n, $2n$) reaction has been determined.[219] The retarding efficiency for neutrons of an aqueous solution of ammonium nitrate has been measured.[229] Its efficiency has also been evaluated, from measurements on other solutions.[230]

ISOTOPICALLY-LABELLED AMMONIUM NITRATE

Isotopically labelled ammonium nitrate is normally prepared with the ammonium nitrogen atom enriched with the ^{15}N isotope, but it can be obtained with the nitrate nitrogen atom enriched.

The enrichment can be achieved because there is a fractionation factor for the exchange reaction between ammonia and ammonium nitrate which has been determined as a function of the dissolved ammonia content. It was found that for a stock ammonium nitrate solution (approx. 60%),

$$\alpha = -0{\cdot}029M + 1{\cdot}034$$

where α is the fractionation factor at 25° and $M = (\text{moles } NH_3)/(\text{moles } NH_3 + \text{moles } NH_4NO_3)$ for the solution.

From these data the equilibrium constant for the exchange reaction

$$\underset{\text{soln.}}{^{14}NH_4^+} + \underset{\text{gas}}{^{15}NH_3} \rightleftharpoons \underset{\text{soln.}}{^{15}NH_4^+} + \underset{\text{gas}}{^{14}NH_3}$$

was calculated to be 1·034, slightly higher than any values previously quoted.[231] Later investigators found the partition coefficient to increase from 1·014 at 5° to 1·025 at 40° and to decrease at higher temperatures.[232] Practical aspects of this method of achieving ^{15}N enrichment have recently been studied.[233] Ammonium nitrate solution was fed at a constant rate to a packed column in which the exchange with ammonia gas occurred. The effects of the nature and size of the packing in the reaction column and of the partial pressure of ammonia were the variables. The isotope separation was improved at low ammonia partial pressures and was affected by the nature and geometry of the packing material. Whereas the isotope enrichment coefficient decreased when the temperature was raised from 20° to 40°, it increased at higher temperatures. This was attributed to simultaneous changes in the enrichment coefficient with the equilibrium constant of the exchange reaction and to the changes in the temperature constants of the reactions in the column with the exchange rate and the molecular proportion of the dissolved ammonia. An apparatus used to obtain an enrichment of 11·4 at.-% of ^{15}N using ammonia and ammonium nitrate has recently been described.[234] A survey[235] concluded that by working on a larger scale by using the chemical exchange process, material much richer in ^{15}N than the 70% assay material at present available could be produced at a fraction of the present cost.

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APPLICATIONS

There do not appear to be any figures available for world production of ammonium nitrate. The largest outlets, by far, for ammonium nitrate are as a fertilizer and for explosives. The fertilizer market especially has expanded rapidly in recent years, in view of the high nitrogen content of the salt. The amount of fertilizer nitrogen supplied in this form exceeded two million metric tons in 1958, for the first time. Thus ammonium nitrate has become as important a source of plant food nitrogen as any other material.[1, 2] The high proportion of nitrogen in ammonium nitrate compared with older nitrogen sources, such as ammonium sulphate, is an advantage.[8] Ammonium nitrate as a fertilizer is used not only alone, but also mixed with other fertilizer materials[2, 3]; this incidentally reduces the fire and explosion hazard[4]; frequently it is given a water-resistant coating.[5] Because of the very high solubility of ammonium nitrate, solutions are frequently used; this procedure is more widespread in North America.[2, 7] The application of ammonium nitrate as a foliar spray has been tried with some success.[6] A number of other references to the use of the salt as a fertilizer relate to special applications or preparative treatments.[9]

Ammonium nitrate is not entirely satisfactory as an explosive; nevertheless, because of its relatively low cost, it is widely used in explosives, particularly for blasting purposes, although it has been much used also in military explosives. Because of the unpredictability of its behaviour, some investigators have reported the salt to be unacceptable as an explosive[10, 11] whilst others have come to the opposite conclusion[11]; much depends on the purpose for which it is required. Its hygroscopicity during storage is a disadvantage, because for explosive use the moisture content of the salt must be less than 0·5%.[11, 12] Explosives can also age owing to double decomposition occurring.[13] To provide a mixture which is reliable in use, ammonium nitrate is mixed with a proportion of a recognized explosive

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substance, e.g. the mixtures with trinitrotoluene which are known as Amatols. Several studies have been made of the suitability of various detonating and sensitizing agents and cover the use of a wide range of organic materials.[14] Attention has been given also to the effect of the physical structure of the ammonium nitrate.[15]

There are many other minor applications of the salt which have been used or proposed. Many depend on the fact that on decomposition the products are entirely gaseous. Controlled thermal decomposition is used to prepare nitrous oxide on a commercial scale and a continuous process has been described.[16] For continuous decomposition it is found best to have a protective film of a mixture of sodium and potassium nitrate on the surface of the melt. Ammonium nitrate has been suggested for use in solid gas-generating rocket propellants,[17] and dissolved in liquid fuels[18]; it has also been tried as an additive to fuels for internal combustion engines to improve combustion characteristics.[19] However, any nitrous fumes in the gaseous products are detrimental to the motor. A method for making casting moulds from charcoal, ammonium nitrate and a resin binding agent has been patented.[20] The mould can be destroyed by combustion after use. Advantage can again be taken of the complete conversion of the salt to gaseous products by using it as a blowing agent. Porous silicate materials can be made from mixtures of silica, an alkali silicate and ammonium nitrate.[21]

The salt can be applied in the preparation of other chemicals. Suggested uses, taken mainly from patents, are: in the preparation of nitrocellulose,[22] guanidine nitrate,[23] sulphonamides,[24] activated alumina,[25] lead oxide[26] and of potassium nitrate from potassium chloride.[27] A process for making ammonium sulphate from calcium sulphate in an ammonium nitrate melt has been patented.[28]

Other miscellaneous uses have been suggested. A concentrated aqueous solution of ammonium nitrate dissolves ammonia more readily than it dissolves carbon dioxide and is used to recover and separate the unreacted gases from the mixture remaining after the synthesis of urea.[29] The salt is effective in stabilizing the colour of vinyl halide resins.[30] Because ammonium nitrate is a repellant for many insects, it can be used to impregnate paper and textile products for protection,[31] but this application is limited by the fire hazard and by the hygroscopicity of the salt. Ammonium nitrate can be used in cartridges for dispersing pesticide materials, which are thermally stable, for fumigating purposes.[32] Ammonium nitrate can be used, with zinc oxide, in the gelation of rubber latex.[33]

Addition of ammonium nitrate to the usual sodium chloride and ice mixture for cooling refrigerated containers gives temperatures 3–4° lower.[34] Solutions can be used to prevent icing.[35] They have also been tested, but not very successfully, for the flocculation of polluted water.[36] Ammonium nitrate can assist in flotation processes in the presence of lime.[37] Solutions of the salt in liquid ammonia are reported to liberate ammonia at a suitable rate to reduce the corrosion of tanks containing sour, crude oils, if the vapour above the two liquids is in contact.[38]

In the laboratory, ammonium nitrate has been used as a turbidity indicator in the determination of water–ethanol mixtures.[39] The presence of ammonium nitrate in the nitric acid layer assists in the separation of uranium by tributyl phosphate.[40] The phase transitions of the salt can be utilized for calibrating the apparatus for differential thermal analysis.[41]

Ammonium nitrate is a convenient source of nitrogen in the fermentation of sucrose to butanol and acetone.[42] The physiological effect of large single doses of the salt has been compared with that of other salts.[43]

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SECTION XVI

AMMONIUM PHOSPHATES

BY W. H. LEE AND M. F. C. LADD

PREPARATION

Ammonium phosphates may be prepared by treating crude calcium phosphate with excess of sulphurous acid and ammonium carbonate. For the production of ammonium dihydrogen phosphate the reaction may be represented by the equation[1]:

$$Ca_3(PO_4)_2 + 3SO_2 + 3O_2 + 2H_2O + (NH_4)_2CO_3 \rightarrow 2NH_4H_2PO_4 + 3CaSO_4 + CO_2$$

Crystalline diammonium hydrogen phosphate of high purity may be produced continuously by passing anhydrous ammonia and relatively pure orthophosphoric acid into a saturated solution of crude ammonium phosphate, at 60–70°, and pH 5·8–6·0. The heat of reaction vaporizes water from the system, and crystals of diammonium hydrogen phosphate separate.[2] Alternatively, the crude phosphate may be purified by adding 10% aqueous tannic acid solution to a 2·0–2·5 M. solution of the phosphate with vigorous stirring, whereby heavy metals such as iron, chromium, copper, and lead are precipitated. The brightness of fluorescence from calcium halophosphate phosphors manufactured from this pure diammonium hydrogen phosphate is not affected by the small amount of organic matter which remains in the solution.[3]

Details of methods for growing single crystals of ammonium dihydrogen phosphate in order to utilize its piezoelectric properties have been given; particular reference is made to the three common defects, veils, tapering, and misorientated overgrowths.[4, 5]

PHYSICAL PROPERTIES

It has been found possible to produce *X*-ray photographs of polycrystalline samples of ammonium dihydrogen phosphate using as little as 1μ-g. of sample.[6]

The specific and molar volumes of solutions of ammonium monophosphate, in relation to its heat capacity, have been investigated.[7] Specific heat capacity measurements have been made on the ternary system potassium dihydrogen phosphate–ammonium dihydrogen phosphate–water.[8]

The thermodynamic data listed in Table I, relating to ammonium phosphates, have been reported.[8a]

Table I.—Thermodynamic Properties of Some Ammonium Phosphates. $T = 298{\cdot}16°$

Compound	State	$\Delta H_f°$	$\Delta G_f°$	$S°$	$C_p°$
$NH_4H_2PO_4$	cryst.	−346·8	−290·5	36·3	34·0
	aq.	−342·9			
$(NH_4)_2HPO_4$	cryst.	−376·1	—	—	43·5
	aq.	−373·6	—	—	—
$(NH_4)_3PO_4$	cryst.	−401·8	—	—	—
	aq.	−394·0	—	—	—

Anomalies in the dielectric constants of anisotropic ammonium dihydrogen phosphate have shown that the phase transition of this salt is seignette-electric in nature. The values of ϑ, the temperature of maximum anomaly near the Curie point, and of the dipole moment, μ, are listed in Table II for a number of such seignette-electrics.[9]

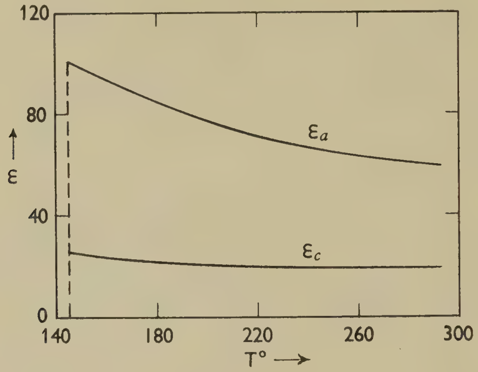

FIG. 1.—Variation of the principal dielectric constants of ammonium dihydrogen phosphate ϵ_a and ϵ_e, with temperature

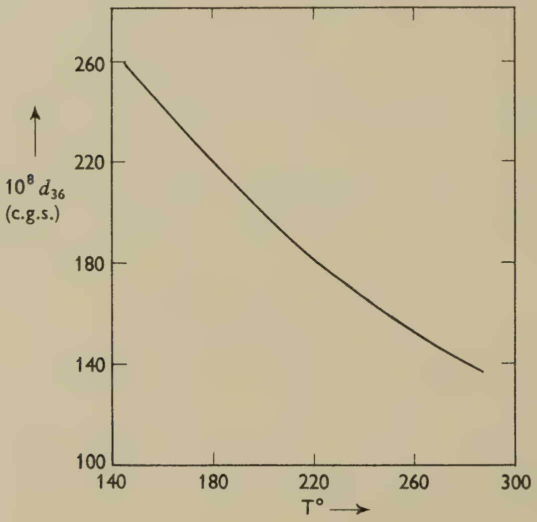

FIG. 2.—Variation of the piezoelectric modulus, d_{36}, of ammonium dihydrogen phosphate with temperature

Table II.—Seignette-electric Properties of Ammonium Dihydrogen Phosphate and Related Substances

	ϑ, °K.	μ, Debyes
$NH_4H_2PO_4$	155	2·77
KH_2PO_4	115	2·04
$NH_4H_2AsO_4$	220	2·74
KH_2AsO_4	91	2·03

The dipole moment is seen to be determined by the nature of the cation, and not of the anion. A further investigation gave $\vartheta = 148$°K.[10]

The variation of the principal dielectric constants of ammonium dihydrogen phosphate, as a function of temperature, has been studied, with the results shown in Fig. 1. The dotted line in this figure refers to the temperature at which anomaly occurs.[11] The piezoelectric modulus is shown, as a function of temperature, in Fig. 2.[11]

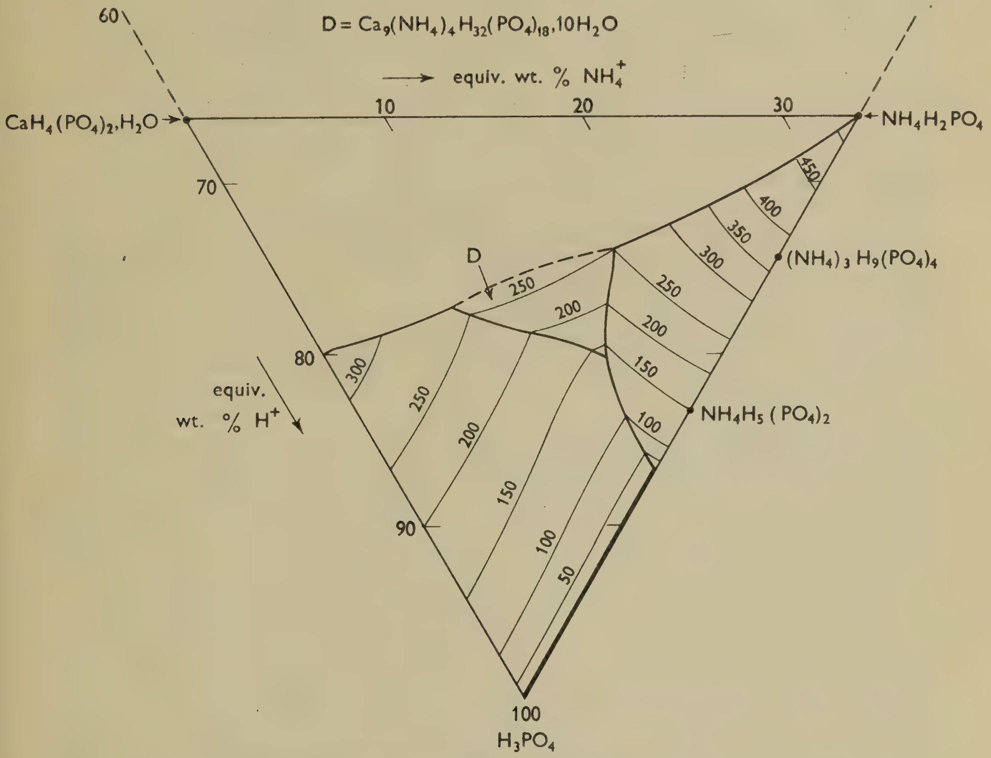

FIG. 3.—The quaternary system Ca^{2+}–NH_4^+–H^+–PO_4^{3-}–H_2O at 25°C. (Contours are labelled in moles of water)

CHEMICAL PROPERTIES

The quaternary system Ca^{++}–NH_4^+–H^+–PO_4^{3-}–H_2O has been studied in the region of the more soluble salts, i.e. in the region having saturated solutions within the composition triangle $Ca_3(PO_4)_2$–$(NH_4)_3PO_4$–H_3PO_4. A new double salt, formulated as $5CaH_4(PO_4)_2,4CaHPO_4,4NH_4H_2PO_4,10H_2O$, falls within this triangle, as shown in Fig. 3.[12] The contours are labelled in moles of water.

USES

Diammonium hydrogen phosphate is a constituent of aqueous fireproofing solutions, suitable for cottons,[13] cellulose fabrics[14] and materials of vegetable origin generally.[15] It is also a constituent of glass-cleaning solutions.[16]

A phosphorescent substance may be prepared by mixing calcium hydrogen phosphate with 10–20% of ammonium cadmium phosphate (prepared by mixing solutions of the two phosphates), and 0·01–2·0% of a manganous salt, followed by heat treatment at 850–900°.[17]

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Complex ammonium phosphates have been incorporated in commercial baking powders.[18] Treatment of abnormal clonal latexes with diammonium hydrogen phosphate reduces the magnesium content, and brings the pH value for gelling down to normal.[19] Ammonium phosphate is effective as an anti-corrosion agent in the production of ammonium nitrate by a modified Solvay process.[20] Diammonium hydrogen phosphate is a constituent of a powdered dentifrice.[21] Ammonium phosphates may be used as catalysts for the isomerization of olefins. For example, a mixture of 30% 1-butylene and 70% *n*-butane is brought into contact with ammonium phosphate on diatomaceous earth at 300°; more than half of the mixture of *n*-butylenes produced is 2-butylene.[22] Polymerization of unsaturated hydrocarbons, amination of olefins, and cracking of paraffins are catalysed by the same material.[23] A 60% $CH\equiv C—CMe=CH_2$, 40% water mixture, passed over an ammonium–chromium phosphate catalyst at 250°, gives an 86% yield of $MeCOCMe=CH_2$.[24]

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SECTION XVII

BIOLOGICAL ACTIVITY OF NITROGEN

BY F. CALL

Nitrogen is a key element for life. It occurs in almost all biologically active compounds, not only in proteins and nucleic acids but also in almost all metabolic co-factors, co-enzymes, vitamins, hormones, etc. Higher animals build these complex molecules from simpler organic molecules which they obtain from their food, while plants are able to utilize still simpler inorganic nitrogen compounds as raw materials. These simple inorganic nitrogen compounds arise in the soil through the operation of the nitrogen cycle. The nitrogen of dead animal or vegetable matter is converted by the action of micro-organisms to ammonium salts which are then transformed by the further action of nitrifying bacteria to nitrates, which is the form in which plants absorb their nitrogen supplies. The inevitable wastages are made good by fixation of atmospheric nitrogen.

The present review is concentrated on the importance of inorganic nitrogen compounds in biology, but it also touches briefly on more complex organic reactions such as transaminations which are being unravelled and elucidated by the use of elegant techniques, e.g., those involving the use of the heavy isotope of nitrogen.

The subject has been sub-divided under the following headings:

1. Nitrogen compounds and food
2. Nitrogen compounds and micro-organisms
3. Nitrogen compounds and plant growth
    (i) Occurrence and distribution in soils
    (ii) The nitrogen cycle in soils
        (*a*) Nitrogen fixation
        (*b*) Immobilization of nitrogen as organic nitrogen
        (*c*) Mobilization of nitrogen
        (*d*) Nitrification
        (*e*) Denitrification
    (iii) Nitrogen compounds as fertilizers
    (iv) Occurrence of nitrogen in plants
    (v) Nitrogen deficiency in plants
    (vi) Absorption of nitrogen by plants
4. Nitrogen compounds and invertebrates
5. Nitrogen compounds and marine or freshwater organisms
6. Nitrogen compounds and vertebrates
    (i) Metabolism of nitrogen compounds
    (ii) Physiological effects of nitrogen gas
    (iii) Anæsthesia by nitrous oxide
    (iv) Toxic effects of nitrogen compounds
        (*a*) Nitrates
        (*b*) Nitrous oxide
        (*c*) Nitric oxide
        (*d*) Nitrogen dioxide
        (*e*) Nitrogen pentoxide
        (*f*) Nitrous fumes
7. Nitrogen compounds and enzymes or proteins

NITROGEN COMPOUNDS AND FOOD

Determination of the total nitrogen and the ammonia-nitrogen in many protein-containing condiments and foods shows that the ammonia-nitrogen may be as high as 25% of the total nitrogen.[1] The nitrogen : sulphur ratio is relatively constant in meat and fish but can vary widely in vegetable products.[2] Ascorbic acid, which is used in the curing of meats to improve colour and flavour, reacts with nitrites in the meat to form nitric oxide which in turn reacts with myoglobin to form nitrosomyoglobin and this imparts a reddish colour to the meat.[3] This nitroso compound dissociates under the action of light and the resulting myoglobin is much more susceptible to oxidation with resultant discoloration of the meat.[4, 5] Nitrous oxide appears to have some value as an antioxidant for shark liver oil.[6] Cream may be stored in nitrous oxide under pressure to retard bacterial spoilage with no subsequent danger to health.[7] Processes have been developed for preparing whipped cream by the sudden release of pressure of nitrous oxide, but the density of such cream is below that of cream prepared by agitation and this results in a low fat content while the bacterial count does not appear to be reduced.[8] A dilute aqueous solution of sodium nitrite was more effective than ice in reducing the spoilage of dressed fish,[27] and hydroxylamine was even more effective.[28]

Bleaching of wheat flour with nitrogen dioxide does not appear to affect the quality of the flour, but the 'agene' process in which flour is bleached by means of nitrogen trichloride has caused considerable alarm and investigation. It was discovered that dogs fed with products prepared from agenized flour developed hysteria and convulsions typified by running fits.[10] The effect was early recognized as being due to the wheat gluten,[11] the acute toxic dose of the agenized gluten being 3·5 g. per kg. for dogs and 10 g. per kg. for rabbits.[12] The toxic effects were found to have a considerable species specificity; thus dogs, cats and rabbits are very sensitive to agenized flour, monkeys show only slight electro-encephalographic abnormalities, while rats, chickens, guinea pigs and man are insensitive.[11, 13, 14] No clinical symptoms or electro-encephalographic changes could be found in human subjects, even in patients with epilepsy, when treated with very high doses of agenized flour.[15, 16] The loss of weight found among rats on a diet of bread made from agenized flour was found to be due to a reduction of palatability.[17, 18] Nitrogen trichloride also produces toxic derivatives when allowed to react with casein, zein, albumin, hæmoglobin or rice protein.[19] Careful investigation resulted in isolation of the toxic factor in a crystalline form[20–23] and its identification, which was confirmed by synthesis,[24, 25] as methionine sulphoxime.[26]

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NITROGEN COMPOUNDS AND MICRO-ORGANISMS

Micro-organisms play a critical rôle in the nitrogen cycle which maintains in the soil an adequate supply of the soluble nitrates essential for plant life and ultimately for all animal life. The inevitable losses of the cycle are replenished by the fixation of atmospheric nitrogen[1, 2, 92–94] by certain specialized micro-organisms which may be symbiotic[95] or asymbiotic. Among the most important species involved in asymbiotic fixation are the *Azotobacter*, in particular *A. chroöcoccum* and *A. vinelandii*.[3, 4] Other species which have been shown to fix atmospheric nitrogen are *Clostridium butyricum*,[5] *Pseudomonas eruginosa*[6] and *Serratia marcescens*.[7] The stable isotope, ^{15}N, has proved invaluable not only for investigating the mechanism of the fixation reaction but also for demonstrating its occurrence.[8] Thus nitrogen fixation has been unequivocably shown to be brought about by the new species *Pseudomonas azotocolligans*,[9] by the photosynthetic bacterium *Rhodospirillum rubrum*,[10] and by the yeasts *Saccharomyces* and *Rhodotorula*,[11, 12] *Chromatium*[96] and *Chlorobacterium*[96]. Only three out of fifteen species of *Clostridia* examined by this technique failed to fix nitrogen.[97] The blue algæ *Anabena variabilis* and *Nostoc sp.* also appear to be able to fix atmospheric nitrogen.[13] Fixation of atmospheric nitrogen by *Azotobacter* is at a maxiumum at pH 7·8 and falls to zero at pH 6·0. Below pH 5·0 irreversible inactivation occurs.[98] The optimum range for fixation is between pH 7·13 and 8·0,[99] and the whole curve is similar to the curve relating growth and pH.[100] Fixation of nitrogen by *Clostridia* appears to be independent of pH between the limits of pH 5 and 9·5[101] and anaerobic organisms may be very important for maintaining the fertility of acid soils.[102] Maximum fixation by *Azotobacter* occurred at 35° under Indian conditions as compared with 28° under temperate conditions and was zero at 10° and 60°.[103] The maximum rate of fixation by this organism occurred at an oxygen content of 4–5% and increased continuously with decreasing oxygen pressure,[104] the respiratory coefficient simultaneously increasing from unity at 5% to 3·5 at 0·1% oxygen.[105] The first product of fixation by *Azotobacter* is ammonia, which is then synthesized into proteins and other complex molecules.[14, 15] The production of extracellular ammonia is probably due to oxidative deamination of proteins and not to direct synthesis from atmospheric nitrogen.[106] Most of the nitrogen fixed by *Azotobacter* is liberated as soluble organic nitrogen compounds.[107] The enzyme system responsible for the reduction of nitrogen to ammonia has been termed 'nitrogenase' and there appears to be some connection between nitrogenase

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and the hydrogenase of *Rhodospirillum rubrum*, because the photosynthetic production of molecular hydrogen by this species ceases in the presence of nitrogen when nitrogen fixation occurs.[10] Hydrogenase has been demonstrated to be present in all of 19 strains of *Rhodopseudomonas* which fixed nitrogen, but the mere presence of the enzyme does not necessarily imply fixation ability.[108] Nitrogenase appears to require molybdenum for correct functioning.[16] Vanadium can replace molybdenum in most species of *Clostridia* and *Azotobacter*[109–111] except perhaps *A. indicum*.[112] The effects of these elements can be detected at concentrations as low as 10^{-11}–10^{-9} M., and thus may form the basis of an extremely delicate analytical test.[109] The optimum pH for nitrogenase and hydrogenase activities are similar, between 7·13 and 7·8, but nitrogenase activity falls to zero at pH 6·0 when hydrogenase activity is still 70% of the maximum value.[113] Nitrogen combines reversibly with the enzyme on a unit basis to form a compound with a dissociation constant estimated as 0·215 ± 0·002 atm.[114] and 0·02 ± 0·005 atm.[115] The intermediate steps, if any, between nitrogen and ammonia are still largely unknown; there is, however, some evidence that hydroxylamine,[17, 18] but not nitramine,[19] is involved in fixation by *Azotobacter*. Hydroxylamine, however, inhibits respiration before inhibiting fixation[116] and accumulates in cultures treated with nitrate in which no fixation is occurring. It may thus be regarded as a secondary product, possibly arising from the breakdown of proteins.[117, 118] Both the anaerobic fixation by *Clostridium* and the aerobic fixation by *Azotobacter* are inhibited by nitrous oxide and carbon monoxide, although assimilation of ammonia is unaffected.[5, 20, 119] Nitrogen fixation is not affected by the presence of the nitrate ion.[15] Inhibition by nitrous oxide is specific and competitive, the dissociation constant for the enzyme–inhibitor complex being 0·08.[4] Nitrous oxide competes with nitrogen in the fixation process alone and is specific to fixation; the nitrous oxide is not utilized by pure cultures.[21–13] Assimilation of nitrogen from labelled nitrous oxide does, however, seem to occur in cultures of *Azotobacter vinelandii* associated with soybean root nodules,[24] while nitrous oxide does not inhibit the utilization of nitrate ion by adapted strains of this organism.[25] On the basis of numerous inhibition studies of fixation by *Azotobacter* it has been deduced that the enzyme has an active surfac area of 2500–3600 sq. m. per mg. of nitrogen fixed, and that carboxyl, amino and carbonyl groups are involved in the active centre.[120–124] A tentative hypothesis of the initial reaction of fixation involves addition of the nitrogen across a diketo group, followed by immediate reduction by hydrogen to form a hydrazine adduct which is capable of reacting with free keto acids, thus producing amino acids.[123]

Ammonia is oxidized to nitrite by several species of micro-organisms, notably *Nitrosomonas* sp. and *Nitrococcus* sp.[124–125] A pH of 8·0 appears to be optimal for this reaction.[126] The free energy of the reaction is utilized by the organism for synthetic purposes and may in fact be the only source of energy.[127] The course of reaction is regarded as proceeding via hydroxylamine and hyponitrous acid, and in some cases hyponitrous acid has been detected by colour tests.[128] The first step in the reaction is, however, still unexplained.[129]

The reverse of this reaction, the reduction of nitrate ion to free gaseous nitrogen, is carried out by a group of organisms known as denitrifying bacteria which includes *Bacillus subtilis*,[26] *Pseudomonas stutzeri*,[26, 27] *P. aeruginosa*,[28] *P. denitrificans*,[28, 29] *Micrococcus denitrificans*,[28] *Denitrobacillus licheniformis*,[28] *Thiobacillus denitrificans*,[30] *Flavobacterium denitrificans*,[31] *Clostridium Welchii*,[130] *Escherichia coli*[131] and several species of *Actinomyces*.[32] *Rhizobium* can reduce nitrates to nitrites but does not appear to be able to carry out further reduction to nitrogen.[33] The actual end products of denitrification appear to depend on certain soil properties such as moisture content.[34] The reduction of nitrate to nitrite is carried out by the enzyme nitrate reductase which has a pH optimum of 5·6, the corresponding optima for the reduction of nitrite being 7·8 and of hydroxylamine 9·0.[132] Nitrate reductase appears to require a reduced alloxazine nucleotide as cofactor,[133] with molybdenum possibly acting as carrier between enzyme and nucleotide.[134] Inhibition of the enzyme by carbon monoxide is reversed by light, suggesting that a ferrochrome type of molecule

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is involved.[135] The actual pathway between nitrate and nitrogen is not definitely known but plausible routes have been proposed.[35] Isotopic techniques indicate that ammonia is an intermediate,[136] while the presence of hyponitrous acid and hyroxylamine has been reported in cultures of *E. coli* which were actively reducing nitrite.[137] Nitrous oxide is produced by many species under certain conditions; it does not appear to be on the direct path of nitrite to nitrogen but rather to be reversibly derived from an intermediate such as nitramide.[27] On the other hand, nitric oxide may be an intermediate with other species.[36, 37] The reduction is coupled with other reactions; thus, succinate as the hydrogen donor may be oxidized completely to carbon dioxide.[29] Under anaerobic conditions the reduction may be coupled with the lactic acid–lactic dehydrogenase system,[36] while molecular hydrogen may be utilized by *Micrococcus denitrificans* under certain conditions[28] and simple sulphur compounds, as well as elementary sulphur, by *Thiobacillus denitrificans*.[30] Pyridine and flavin nucleotide stimulate reduction by *Flavobacterium denitrificans*, metal-binding agents such as cyanide and salicylaldoxime being inhibitory.[31] As might be expected the rate of dentrification is dependent on the pH value.[38] It has been suggested that the relative proportions of nitrogen and oxygen in the earth's atmosphere may depend on a balance between the action of nitrifying and that of denitrifying bacteria.[39]

Many species of bacteria are able to synthesize proteins from simpler nitrogen compounds, others to degrade proteins to simple molecules.[40] A number of species are found to deaminate glycine to glyoxylic acid in a slightly alkaline medium.[41] It is believed that amino acids may be formed by the condensation of ammonia with an α-keto-acid.[42] The respiratory coefficient of *Aspergillus oryzæ* varied with both the carbon source and the nitrogen source, being greater with nitrates than with ammonium salts.[43] Localized corrosion of limestone has been attributed to the production of acid by nitrifying and denitrifying organisms.[44]

Micro-organisms are of great importance in the treatment of sewage to render it innocuous. The actual loss of nitrogenous compounds in sewage may be serious in some countries; thus it is calculated that the loss in sewage from the major cities of India is equivalent to 425 tons of ammonium sulphate per day.[45] A number of treatments have been developed for removing fertilizing elements from sewage,[46, 47] but the most successful to date appears to be the activated sludge process. This process can be operated under such conditions that there is no loss of nitrogen by formation of free ammonia or nitrogen. The presence of nitrates appears to result in a smaller loss of nitrogen.[48] Nitrification is in fact not essential to the process.[49, 50] The carbon : nitrogen ratio is important, oxidation increasing as the ratio is reduced; the ideal ratio is about 5·7 : 1.[51–53] The actual nitrogen transformations occurring in the sludge affect its pH value.[54] The chief organism taking part in the purification process is *Zoöglea ramigera*,[55, 56] but protozoa are also present[49, 57] and a pure culture of *Sphaerotilus* has been successfully used.[58] Nitrifying and denitrifying bacteria play an important part in the purification of rivers polluted with sewage,[59, 60] while the particular distribution of nitrogen compounds with depth in the Black Sea is also attributed to similar micro-organisms.[61]

The nitrogen nutritional requirements of micro-organisms have been reviewed.[62] Many bacteria are able to utilize simple nitrogen compounds as the sole source of nitrogen, some species using ammonium chloride, sodium nitrite or sodium nitrate with equal efficiency.[63] In some cases adaption plays an important rôle in deciding the nitrogen source. Thus, from a parental strain of *Escherichia coli*, which is strongly inhibited by nitrite or nitrate ions, a strain has been isolated which uses these ions as the sole source of nitrogen.[64] *Azotobacter* has preformed enzyme systems capable of assimilating ammonia, and the cells must adapt themselves to the utilization of nitrate or nitrite.[138] The assimilation of nitrate and nitrite by this species is a zero order reaction, the rate of which increases directly with the rate of oxygen consumption.[139] In contrast the rate of uptake of nitrate by *E. coli* is inhibited by oxygen.[140] The anion of ammonium salts may be important; thus of a series of ammonium salts used as the sole nitrogen source for *Bacillus subtilis*, the lactate is the best, citrate and butyrate less satisfactory, while the chloride and sulphate are

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unsatisfactory probably because of the development of low pH.[65] Yeasts make much better growth when supplied with amino acids than with simple nitrogen salts.[66] Ammonium salts stimulate the respiration of bakers' yeast, and part of the ammonium ion is taken up and synthesized into nitrogen compounds.[141] Ammonium ions are also a specific catalyst for the synthesis of pantothenic acid by yeast.[142] Isotopic studies show that ammonia is taken up by the yeast *Torulopsis utilis*; this nitrogen does not however appear to be synthesized into higher compounds such as proteins but to be held separately.[67] The rate of production of citric acid by moulds depends on the nitrogen source, being greater for mineral nitrogen than for organic nitrogen compounds.[68] The production of penicillin[69, 70] and of streptomycin[71, 72] also depends on the type and amount of nitrogen available, while the activity of proteolytic enzymes is much greater in *Penicillium* supplied with nitrate than with organic nitrogen.[73] The effect of thiourea on *Aspergillus niger* depends on the type of nitrogen source.[74] Most of these fungi appear to synthesize glutamine and asparagine from either nitrate or ammonia as nitrogen source.[75] Fungi can in some cases be separated into groups according to the nitrogen nutritional requirements.[76] Protozoa tend to require more complex organic nitrogen molecules, but can to a limited extent be adapted to utilize inorganic sources.[77–79] A great deal of work has been done on the utilization of complex organic nitrogen compounds for the growth of micro-organisms and in some cases the results are used as a means of generic classification of different strains.[80] The two optical isomers of amino acids are usually utilized by micro-organisms at different speeds; the naturally occurring isomer is usually accepted more readily by the majority of species, but this is by no means true in all cases.[81, 82]

A mixture of oxides of nitrogen, such as is produced by the passage of air through an electric arc, has powerful bactericidal properties.[83] This effect is probably due to the presence of higher oxides, since nitrous oxide has little effect at atmospheric pressure, although it too is an effective bactericide at pressures of 28–50 atmospheres in the absence of air.[84, 85] Nitrous oxide is a strong inhibitor of hydrogenases, such as those which occur in *Hydrogenomonas facilis*[86] and *Proteus vulgaris*.[87] Nitrogen trichloride has been used successfully for the sterilization of water, sewage and milk[88] and for fumigating cantaloupes,[89] oranges[90] and lemons[91] against both stem-end rot caused by *Diplodia natalensis* and blue and green moulds due to *Penicillium sp.*

Nitrites inhibit the growth of many obligates and facultative anaerobes[143] and induce mutations in many species of *Aspergillus*.[144] Exposure to low concentrations of nitrous acid inactivates many viruses,[145] and destroys the power of attachment of T.2 bacteriophage to the host cells, possibly by reaction with amino groups present in the virus.[146] Low concentrations of sodium azide exert a selective bacteriostatic action on many gram-negative organisms and fungi.[147–148] There may be correlation between this bacteriostatic action of azide and the ability of the organism to reduce nitrates.[149] Azide stimulates the respiration of yeast at low concentrations but inhibits it at higher ones.[150] The exact mechanism of inhibition of respiration is not known with certainty, but the site of action may be a dehydrogenase.[151] It was observed that the catalase content of many micro-organisms is reduced by azide.[152]

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NITROGEN COMPOUNDS AND PLANT GROWTH

Occurrence and Distribution in Soils

DETERMINATION OF SOIL NITROGEN

A number of reviews have appeared of the literature dealing with various aspects of the distribution and economy of nitrogen compounds in soils[1-8]; of these the last reference is the most recent and perhaps the most valuable.

The most realistic method of determining the soil nitrogen available to plants is by growth of an actual crop and there have been many attempts to devise a more rapid biological test based on plant growth. The earliest and the best known of these tests is the Mitscherlich pot test.[9, 10] A very rapid modification is the observation of the growth of the fungus *Cunninghamella* on the soil under test.[11] Other suggested methods depend on determination of the chlorophyll content[12] or the invertase activity[13] of rye seedlings grown in controlled conditions by the Neubauer procedure or on the hydrogen cyanide content of sorghum plants,[14] since the production of all these substances has been found to depend closely on the amount of nitrogen available to the seedling. The Hoffer method of assessing the nitrogen requirements of the soil by chemical tests on the nodes and internodes of corn stalks has been found to be less reliable than judgment of leaf coloration.[15] Although Lundgardh's method of leaf analysis may give a good indication of the status of nitrogen in the soil,[16] the method does appear to be unduly dependent on soil type and may give misleading results in some cases.[17-19] The occurrence of nitrogen in different forms in soils has led to the development of many different methods for the determination of available nitrogen in soils. A modified Kjeldahl procedure has been widely used[20, 21] while the König–Hasenbäumer method, which determines the nitrogen soluble in 1% potassium sulphate solution, is said to be reliable.[22] Mineral nitrogen (ammonia, nitrate or nitrite as opposed to combined organic nitrogen) has been determined by extraction with N-calcium chloride solution.[23] The various chemical methods for the determination of nitrate and nitrite have been compared and found to give good agreement.[24] A procedure has been developed for the determination of the various forms of nitrogen present in a soil using a single 1 g. sample.[25] A close relationship has been observed between the total nitrogen content of soils and the chlorine index as found from the loss of chlorine when the soil is treated with sodium hypochlorite.[26] Nitrate-nitrogen appears to be an index of the nitrogen requirement of a growing crop.[27] Although the accuracy of chemical methods is high, the great variability of soils makes it essential both to take care in the selection of samples and to analyse the results statistically for significance.[28-31] It is believed that analysis of samples of wet soils gives a truer picture of the available nitrogen than does analysis of air-dried or oven-dried samples.[32]

THE CARBON-NITROGEN RATIO

Considerable importance has been ascribed to the organic carbon–nitrogen ratio (C:N) as a measure of soil fertility.[33] Although in some investigations no close correlation can be found between the C:N ratio and soil productivity,[34] in other cases the correlation is high.[35] While both carbon and nitrogen may show marked increases after several years cultivation, the C:N ratio is usually found to be remarkably constant.[36] Observed extreme values are 3·5 and 35 but relatively few values lie outside the limits 7 and 15, the mean value being 10.[37, 38] The mean values for various soil types are: chernozem, 9·0; prairie, 12·2; podzol, 12·6; and laterites, 15·2.[39] The ratio is a measure not only of the availability of organic matter as food for micro-organisms but also of the micro-biological activity of the soil, since a high ratio may increase the growth of bacteria at the expense of moulds.[40] A ratio of 20 indicates a fair supply of available organic matter, while one of 10 implies that decomposition of the organic matter is well advanced.[37] The action of micro-organisms is to reduce the ratio as the carbon is metabolized and oxidized to carbon dioxide and the nitrogen assimilated into bacterial proteins. The nitrogen may thus be fixed and not available for plants until the C:N ratio is still further reduced to the point at which the organic nitrogen is converted to nitrate.[41–44] The type of organic matter is also important, lignins causing release of the nitrogen as nitrate at a higher ratio than does starch or cellulose. Nitrogen fixed biologically by adding cellulose, starch or straw to the soil remains fixed for 2½–3 months, after which it is converted into a form available to plants even at a ratio of 30.[45, 46] Although acidity increases the C:N ratio because of the loss of nitrogen,[47] liming appears to have no effect on the ratio.[48] Certainly nitrification ceases in acid soils at a lower ratio than in alkaline soils.[49] Results from many different countries suggest that the ratio also increases with the soil temperature.[50] The 'bolting' of cotton in some Australian soils has been associated with a C:N ratio of 7·0 to 8·5.[51] There are indications of a similar close relationship between the soil nitrogen and certain phosphorus fractions[52] and also soil organic sulphur.[53, 54]

The amounts of available nitrogen occurring in the top 12 in. of soil vary considerably throughout the season; thus extreme values of 5 and 53 lb. per acre have been found for ammonia nitrogen and 6 and 56 lb. per acre for nitrates.[55] In general the various forms of nitrogen decrease with increasing depth of soil, but the C:N ratio may either decrease[56] or increase.[57] Total nitrogen tends to increase in the surface soil with increase of elevation of the site above sea level.[58] In south eastern France the largest amount of inorganic nitrogen is found in the soil between 2 and 6 cm. deep, and there is some experimental evidence that this maximum may be related to the soil temperature of this layer.[59] Although there appears to be no relationship between soil nitrogen content and the degree of water-stable aggregation,[60] soil aggregates between 1 and 10 mm. in diameter are richest in nitrogen and contain the largest number of bacteria.[61] Soil from the tops of ridges in irrigated fields has been found to contain twice as much total nitrogen and 50–100 times as much nitrate as the soil in the adjoining furrows.[62]

FACTORS WHICH INFLUENCE THE SOIL NITROGEN CONTENT

The movement of nitrogen in soils appears to depend on the form in which the nitrogen occurs. Thus ammonia tends to be rather immobile, since it is absorbed by a cation complex while nitrates move freely with the soil moisture.[63] Prolonged dry weather causes the nitrates to move upwards to the surface of the soil where they are not available to plants. Subsequent rain may cause losses by run-off or may carry the nitrates downwards into the root zone again.[64] In lysimeter tests 40–50% of the nitrates produced during the year may be lost by leaching.[65] On a silt loam 53% of the total annual loss occurred during spring and only 5% during winter,[66] but at another site of the same soil type almost all the loss occurred during winter.[67] Loss of nitrogen by leaching decreases as the clay content increases, but this effect is ascribed to differences in the rate of decomposition of organic matter in the soils rather than to differences in the rates of percolation.[68] Nitrates supplied as sodium nitrate may be entirely leached from the surface layers in periods of six weeks to four months depending on the rainfall.[69] Loss of ammonium nitrogen from flooded soils may be very great, but the loss depends on the pH value and on the temperature and in some conditions is negligible.[70, 71] In some soils and climates the loss of nitrogen by leaching may be counterbalanced by the fixation of atmospheric nitrogen, so that the nitrogen content may remain at a steady value for many years.[72] Owing to reduced losses by leaching, fertilization by ammonium salts may result in a greater carry-over of available nitrogen than does fertilization by nitrates.[73] The presence of a crop also seems to reduce leaching of nitrogen compounds[74–76] and this effect depends on the extent of the root system.[77] There is some evidence of a greater net upward movement of nitrogen compounds in soils lying under grass, so that the top soil tends to gain nitrogen.[78] The soil eroded by surface run-off from a black organic soil is largely the silt fraction which was found to be much richer in nitrogen than the remaining soil.[79] The nitrogen content of any given horizon is found to depend on the position on slopes, the contents near the tops of ridges being lower than on the lower slopes.[80, 81]

The fixation of soil ammonia depends partly on the soil texture, partly on acidity and partly on the nature of the clay minerals or base exchange complex.[196–197] Considerable fixation occurs when the predominant clay mineral is illite or vermiculite, and most montmorillonite clays have little tendency to fix ammonium ions.[198, 199] The simple equation of mass action did not apply to all soils at all ionic concentrations in the exchange of potassium and ammonium ions, and a better fit was obtained by introducing the theory of mixed crystals.[200] The free energy and heat content of this exchange have been calculated from an exchange equation.[201] The fraction of fixed ammonia available to nitrifying bacteria varies inversely with with the degree of fixation, vermiculite or illite-type clay minerals thus giving the lowest nitrification.[202] Ammonium ion has been observed to cause a visible crusting of the surface soil, persisting for some months after treatment with ammonium salts.[203]

The nitrogen content of soils is markedly dependent on climate and a steady decrease is observed in average values in the soil from north to south of the United States, indicating that soil nitrogen decreases with increasing temperature.[82–84] A relative humidity of 40–70% and a temperature of 34–38°C. are regarded as optimal for the accumulation of nitrates in cultivated desert soils.[85] In tropical soils a higher proportion of the total nitrogen is available to plants than is the case in temperate soils.[86] The nitrogen content of temperate grassland soils is observed to increase logarithmically with humidity although humidity has no influence in sub-tropical timber soils.[87] An empirical equation has been derived for the dependence of the total nitrogen content of the soil N on the humidity factor H, and temperature T:

$$N = C\,\mathrm{e}^{-k_1 T}(1-\mathrm{e}^{-k_2 H})$$

where C, k_1 and k_2 are constants.[88] In many tropical soils there is a rise in nitrogen content during the onset of the rainy season which may be followed by a fall in the wettest period. This trend is clearly due to a balance between the activity of the micro-organisms and losses by leaching.[89–91] The nitrogen content often fluctuates greatly even from day to day, and a clear consistent relationship between nitrogen content and humidity may not be found.[92] The total nitrogen content of some rice soils is found to increase by about 25% after flooding.[93] Ammonia tends to be produced at a higher rate in swamp soils than in dry soils,[94] while damping a soil is found to result in increased ammonia and nitrate contents.[95] In some Indian soils the amount of atmospheric nitrogen fixed is directly related to the water content of the soil.[96] Nitrifying activity in a black cotton soil reaches a maximum at a moisture content of 24–30%.[97] Seasonal variations occurred in a cropped and bare peat soil, the changes being in opposite directions in the two cases. The cropped soil restored its reserves during winter and spring.[98] In a Mediterranean soil the nitrogen content, which was mainly in the form of nitrate, reached a maximum during August and September.[99]

Normal rain and snow contain small but definite amounts of nitrogen compounds and the annual contribution to the soil from this source is not inconsiderable. Analyses at a number of sites ranging from temperate to tropical latitudes indicate that there is likely to be added each year to the soil from natural precipitation between 4 and 12 lb. per acre of ammonia and between 1 and 7 lb. per acre of nitrates.[100–111] In general rain water in winter contains a higher concentration of ammonia than of nitrates or nitrites, which are chiefly produced by lightning discharges.[106] Typical figures, averaged over two years, for the concentrations of nitrogen compounds in rainwater are[111]: nitrite 0·002–0·008 mg./l., nitrate 0·07–0·08 mg./l. and ammonia 0·6 mg./l. The concentration of both ammonia and nitrate is stated to decrease in a logarithmic manner as precipitation continues.[112] Rainfall collected under a tree was found to be much richer in nitrogen compounds than rain collected in a nearby clearing.[113] The formation of nitrates by thermonuclear explosions has also been discussed.[114]

The nitrogen content of soils is greatly dependent on the cultivation practice. Thus plots cultivated for 53 years without fertilization suffered a total loss of over a ton of nitrogen per acre (2550 kg./hectare),[115] while prairie soils brought under cultivation lost 33% of their nitrogen after 14 years, mainly by leaching of nitrate to depths beyond those of root penetration.[116] The rate of loss of nitrogen usually decreases markedly as the nitrogen content becomes low.[117] Treatments of the soil with soil fumigants such as DD (a crude dichloropropene formulation) or ethylene dibromide tend to cause partial sterilization and changes in the relative population of micro-organisms, the net result being to increase the nitrogen available to plants.[118] Similar results have been observed after treatment of soils with carbon disulphide,[204] chloropicrin[205] and most effectively of all by steam sterilization.[205] The first effect is an increase in the ammonia nitrogen due to a stimulation of nitrogen fixation and suppression of nitrification. After about two months the additional ammonia begins to be converted to nitrate.[205, 206] Although the concentration of ammonia is uniform with depth there is an accumulation of nitrate at the surface of the soil due to the upward movement of moisture.[207] Liming appears to increase the loss of soil nitrogen,[119, 120] but the increased plant growth resulting from the treatment may tend to conserve nitrogen.[121] Tillage operations may increase the loss since stirring the soil increases the rate of loss of gaseous nitrogen compounds.[122] The improved soil aeration may increase nitrate formation with possible loss by leaching.[123, 124] There is in fact high correlation between nitrate formation and rate of loss of nitrogen. The increased erosion due to cultivation up and down a slope may cause much higher losses than cultivation across the slope.[125] Delayed spring ploughing has been found to result in decreased water supply and hence a decrease in soil nitrates with consequent decrease in crop yield.[126] Application of a nitrogen fertilizer alone causes a nitrogen loss much greater than that occurring in the unfertilized and cultivated soil, although the potassium and phosphates of balanced fertilizers have a favourable action on the nitrogen balance of soils.[127] Continual removal of the surface litter from forest soils reduces both the total nitrogen and nitrate content.[128] Although annual burning of pastures reduces the nitrogen content of the soil,[129] annual burning of a forest plot had no adverse effect.[130] Crops differ greatly in the amounts of nitrogen they remove from the soil.[131] Soil under grass gains nitrogen and may show a much greater nitrogen content than unfertilized,[132, 133] bare soils. Similar gains are shown by soils under alfalfa.[134] Legumes are well known to increase the nitrate content of soils. The effect persists for 2–3 months after harvesting the legumes because of stimulation of bacterial activity.[135–136] Black locust roots contain nitrogen-fixing bacteria and stimulate the growth of adjacent plants.[137] Cover crops had no effect on the nitrogen content of orchard soils,[138] whereas cover crops of *Indigofera endecaphylla* appeared to be effective in maintaining and even increasing the nitrogen content of soils in tea plantations.[139] Cereals make considerable demands on soil nitrogen and maize by far the greatest, the decrement under maize being twice that under any other grain.[140] Similarly the nitrogen content of soil supporting red gum and yellow poplar was twice as high as that of soil under shortleaf pine.[141] Weeds also make a heavy drain on the nitrogen resources of soil and the nitrate content of a bare soil was found to be fifty times as high as the same soil under weeds.[142] The nitrogen content of poor land can in fact be increased considerably by allowing weeds to grow and ploughing them in each year.[143] It has been found that the nitrogen needs of grain crops may be met by a four-year rotation, in which nitrogen is accumulated during the period under grass,[144] although the nitrogen content of soil under permanent grass may be 50% higher than that under the rotation.[145] Grain followed by summer fallowing reduces the soil nitrogen because of the loss of organic carbon.[146] In general the decrease in soil nitrogen is reduced as the length of rotation increases, 5 years rotation being better than 3 years,[147, 148] although some soils show a continuous loss regardless of cropping system or fertilizer treatment.[149] Row crops cause greater losses of nitrogen than grain crops.[150, 151] The best method of conserving the fertility of land thus appears to be to alternate grain with legumes which are ploughed in each year, or to combine rotation and livestock farming.[152, 153]

The process of green manuring with or without the addition of nitrogenous fertilizers is an important factor in the nitrogen economy. The green manure supplies

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carbon compounds to adjust the carbon:nitrogen ratio to the correct value for the optimum action of the soil micro-organisms and thus enables more efficient use to be made of the available nitrogen. Between 92 and 95% of the total nitrogen may be accounted for in the crop and the soil.[154] The nitrogen of the green manure is also slowly utilized; thus in 18 months 82·5% of the nitrogen of *Crotolaria striata* and 91·6% of that of Natal grass passed into the soil solution.[155] At carbon:nitrogen ratios greater than about 35:1 nitrogen may be inactivated by being synthesized into organic compounds.[156] A number of studies have been made of the action of straw and other organic additions in preventing the loss from soils of added nitrogen. The most important factors are the nature of the nitrogen source and of the organic matter. The cellulose fraction of the straw serves to supply energy to the micro-organisms, while the lignin fraction acts as a buffer for the absorption of ammonia and also combines with proteins to give very stable complexes.[157, 158] Ammonium salts or nitrates appear to be necessary for the decomposition of straw, less being required under anaerobic conditions.[159] Depending on the carbon:nitrogen ratio[160] the mineral nitrogen may be immobilized[161, 162] or the soil organic nitrogen may be mineralized,[163] but both processes take place very rapidly, in fact within two days. When summer legumes are ploughed in a large loss of nitrogen often occurs owing to winter leaching of the nitrates formed; the loss may be much reduced by delaying the ploughing-in until the following spring.[164] Nitrate formation occurs mainly in the lower layers of a mulch of straw or hay rather than in the soil, and the upper limit of carbon:nitrogen ratio for nitrate production appears to be about 15:1.[165] The utilizable nitrogen of stable or other animal manures appears to be the free ammonia-nitrogen and the organic nitrogen is not used during the first year.[166] Of this ammonia-nitrogen 56–66% is used by plants as compared with 63–77% of the available nitrogen of mineral fertilizers.[167] During the first month or so after application of animal manure, biological fixation may actually reduce the amount of mineral nitrogen available to plants. After 12–18 months this organic nitrogen may be broken down and the free nitrate increases greatly.[168] Under Indian conditions the rate of nitrification and of nitrate accumulation was in decreasing order: ammonium sulphate, green manure, cattle manure, but loss of nitrogen was greatest in plots fertilized with ammonium sulphate.[169] Also in India the nitrogen content of a soil was doubled by the application of cow dung, but was unchanged by the addition of ammonium sulphate.[170] In New Zealand, however, the effect of returning dung and urine to the soil was completely masked by the effect of clover growing on the pasture.[171] Successful composting appears to require a carbon:nitrogen ratio of 10 or 12:1, otherwise excessive losses of nitrogen may occur. Addition of a little soil reduces these losses greatly.[172, 173] The loss of gaseous ammonia from stored animal manure, which may reach 60% of the initial total nitrogen content in a few months, may be prevented by adding a small proportion of powdered sulphur[174, 175] or of superphosphate.[176] Among materials suggested for use as organic manures are fungal mycelia from the fermentation of molasses,[177] hair, wool or leather,[178] domestic sewage,[179] activated sludge,[180] coal or lignite[181] and peat.[182]

NON-PROTEIN NITROGEN

Not all the nitrogen in organic soils is determinable by the Kjeldahl method, and the Dumas method may give a considerably higher percentage of total nitrogen, indicating that an appreciable fraction of the organic nitrogen may be of non-protein nature.[183] A number of different schemes have been proposed for fractionating the organic nitrogen compounds of soils.[184–186] Soils contain considerable quantities of protein which may be hydrolysed into its constituent amino acids. The non-basic amino acids tend to decrease during nitrification or growth of a crop.[187] The protein hydrolysates contain the commonest α-amino acids, but differ from those of plant proteins in yielding no sulphur-containing acids and very little arginine or histidine.[188–190] Much of the organic matter of plant litter, and chiefly the lignin, fix considerable amounts of ammonia while undergoing auto-oxidation. The proportion of lignin oxidized depends on the pH value.[191] Glucose, fructose, di- and tri-hydroxyphenols and tannic acids also fix ammonia. The product is a humus-like material which is very stable to acids.[192] This humin-nitrogen is non-protein nitrogen and probably occurs in complex, heterocyclic nitrogenous compounds.[193] Between 24 and 37% of the total soil nitrogen is α-amino nitrogen and is derived from some type of protein. Positive tests are obtained also for amino sugars.[194] The ratio of the soil protein nitrogen to the total organic nitrogen has been proposed as a sanitary index of the extent of contamination of the soil by decaying organic matter such as fæces. Ratios below 0·7 indicate heavy contamination while 0·98 indicates none.[195]

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The Nitrogen Cycle in Soils

A number of useful reviews of and discussions on the nitrogen cycle in soils have appeared.[1–10]

NITROGEN FIXATION

Little work has been done on symbiotic nitrogen fixation, which is carried out by bacteria associated with the nodules formed on the roots of leguminous plants.[11] Such fixation does not appear to be influenced by the actual nitrogen content of the soil and occurs in a soil containing 3000 lb. of total nitrogen per acre.[12] In alfalfa, however, the infection of the nodules and the establishment of fixation appear to require a supply of combined nitrogen, and the amount of nitrogen fixed during the crop is inversely proportional to the amount of soluble nitrogen available to the plants. Soya beans behave similarly but less nitrogen is required initially.[13] The use of the stable isotope, ^{15}N, indicated that fixation does occur in the nodules and that the combined nitrogen thus formed is rapidly transferred to other parts of the plant.[14] The particular strain of plant has an important influence on nodule formation.[15] The activity of *Rhizobium trifolii* increases with the partial pressure of the nitrogen up to 0·15 atm. and thereafter is independent. Oxygen affects mainly the carbohydrate metabolism of the host plant, while hydrogen has an inhibitory effect on symbiotic fixation but does not affect non-symbiotic fixation by *Azotobacter*.[16] It has proved difficult to demonstrate with certainty nitrogen fixation in excised root nodules of leguminous plants, but by using isotopic nitrogen a very rapid fixation has been found.[95] Conditions inside root nodules are largely anaerobic and respiratory activity is less than that of the adjacent roots.[96] Nodules have been found to contain a red hæmoglobin which has been named 'leghæmoglobin'; it is essential to fixation of nitrogen. Leghæmoglobin is synthesized by the plant and is converted to an inactive green pigment when the plant ceases to grow or is transferred to the

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dark.[97–99] Hydroxylamine has been isolated from systems undergoing fixation, though the failure of hydroxylamine to exchange with isotopic nitrogen is adduced as an argument against its being an intermediate in the process.[100] During early growth the bulk of the nitrogen leaving the nodules is in the form of aspartic acid which could be formed by the reaction of hydroxylamine and oxalacetic acid.[101] A tentative hypothesis for the fixation by nodule bacteria involves the reaction of nitrogen with a diketo group in the enzyme responsible.[102] Clover plants inoculated with free-living species of rhizobia die, since the nitrogen synthesized is not in a form assimilable by the plant.[103]

Chemical methods of estimating soil nitrogen, such as the Kjeldahl method, are not sufficiently sensitive to measure asymbiotic nitrogen fixation with certainty,[17] but the use of isotopic nitrogen has conclusively demonstrated such fixation by *Azotobacter vinelandii*, *Nostoc muscarium* and *Clostridium pasteurianum*.[18] The suggestion that the blue-green algæ are directly or indirectly involved in nitrogen fixation is not proven, and the evidence seems to be against it,[19–21] The maximum activity of *Azotobacter* occurs in soils having pH values of 6·5–7·5 and the organisms may not survive at a pH below 6·0.[22–24] Animal manures may aid fixation, but the effect may be less important than that of the pH value in some soils.[22, 25] Molasses is an excellent fertilizer in tropical countries in increasing nitrogen fixation by *Azotobacter*. Although the number of this organism is reduced in soils exposed to strong sunlight, fixation is often increased.[26, 27] The optimum temperature for nitrogen fixation and oxidation of organic matter in the dark is 35°.[104] Moist soil conditions favour fixation,[28, 29] as does liming, which also seems to have a specific stimulatory effect on nodulation in addition to reducing the acidity.[30] The soil type also appears to be important, much greater fixation occurring in clay loams than in sandy loams.[31] Fixation increases in soils saturated with iron salts.[32] In the 'spotty' condition in wheat fields, the soil in the spots contains appreciably more nitrogen in the form of nitrates available to plants even though the plants remove much greater quantities. It has not been possible, however, to prove that nitrogen fixation occurs more rapidly in the spots.[33] There is some evidence that fixation of nitrogen by *Azotobacter* may be stimulated by secretions from the growing roots of seedlings.[105, 106] Analysis of thermodynamic data suggests that the overall fixation reaction coupling oxidation of glucose and reduction of elemental nitrogen to ammonia may not be endothermic, as is usually assumed.[107]

IMMOBILIZATION OF NITROGEN AS ORGANIC NITROGEN

When soils are treated with sugars or starch there occurs a rapid build-up of a heterotrophic microbiological population and nitrogen is immobilized in organic forms. The population declines when the organic carbon is used up and ammonia is formed once again by lysis of the dead cells.[34] The micro-organisms show a marked preference for ammonia,[35] but some nitrate is always utilized, the pH value of the soil falling or rising as the former or the latter is used predominantly. A linear relationship exists between the amount of carbon added and the amount of nitrogen immobilized, approximately 1 unit of nitrogen being immobilized for every 9 units of carbon.[36] Very considerable fluctuations may occur in the organic nitrogen content of soils under different conditions of cropping.[37] Addition of powdered forest leaf-fall to an African soil caused complete and rapid disappearance of nitrate for at least 10 weeks.[38] Deciduous trees appear to favour a high organic nitrogen content, whereas the reverse is true for conifers. There is also some evidence of a relationship between the calcium and nitrogen contents of the organic matter.[39]

MOBILIZATION OF NITROGEN

The mobilization of organic nitrogen as mineral nitrogen appears to be a general property of all soils and is controlled by the food supplies available to the micro-organisms.[40] The optimum moisture content for mobilization is between 34 and 50% of saturation of the soil. Both aerobic and anaerobic processes appear to occur during mobilization, the former process favouring ammonification.[41] Mineralization of the organic nitrogen is increased at higher temperatures[42] and at lower pH values.[43] Addition of such acidifying substances as sulphur, alum or ferrous sulphate thus increases the rate of ammonia production.[44] A definite seasonal variation of mineralization has been demonstrated and the supply of ammonia and nitrate usually balances plant needs in cultivated soils, but in swampy soils mineralization tends to be low at the times when plants require nitrogen and high when growth has ceased so that considerable nitrogen wastage occurs.[45] A narrow carbon:nitrogen ratio is required for ammonification, but in tropical conditions this may lead to loss of nitrogen as gaseous ammonia.[46] Cellulose is decomposed in soils by fungi such as *Trichoderma* and *Penicillium sp.*, and nitrogen is assimilated by the fungal hyphæ. These fungi prefer ammonia but are able to utilize nitrites.[47, 48] Equations have been derived for the determination of rates of mineralization and immobilization of nitrogen in soils by means of isotopic tracers. Preliminary data indicate that the law of mass action is applicable to the reactions.[108]

NITRIFICATION

Nitrification of ammonia proceeds via the nitrite and takes place only when the soil has an optimum moisture content. When the soil is brought to this optimum, nitrite rapidly builds up to a maximum and then falls again while nitrate begins to increase as nitrite decreases.[49] There is no immediate accumulation of nitrate after treating a soil with ammonium sulphate, although nitrites may be present, but after incubation of the soil nitrification proceeds rapidly, indicating that the necessary micro-biological population has been built up.[50] The rate of nitrification follows a sigmoid curve unless the soil is saturated with the necessary nitrifying bacteria, when the rate is linear. Nitrification occurs wholly at the soil surfaces where ammonium ion is adsorbed, and the concentration of this ion in the soil solution has no effect on the rate of nitrification.[109] Nitrification is reduced by treating the soil with highly carbonaceous materials such as straw, and a narrow carbon: nitrogen ratio seems to be necessary.[51, 52] The influence of cropping is, however, much greater that that of added organic materials, probably because of the greater microbiological activity in the rhizosphere.[53] Nitrification is also favoured by high pH values and good aeration of the soil,[54] though the nitrate produced tends to reduce the pH value and increases the oxidation-reduction potential.[55] Anhydrous ammonia or glycine injected in soils is nitrified more rapidly than ammonium salts in slightly acid soils and less rapidly in neutral or alkaline soils.[110–112] Recovery of the nitrogen of amino acids as nitrate decreases with increase in the carbon: nitrogen ratio of the amino acid. Methionine and thiourea have definite inhibitory action on nitrification.[112] There is no evidence that carbon dioxide has any direct effect on nitrification.[56] Nitrification does proceed more rapidly in the presence of calcium ions which probably serve as a base to fix the nitrate formed; aluminium is not able to replace calcium in this respect.[57, 58] Neutral sodium salts have a stimulating action on the nitrification process.[59] Although light has no effect on ammonification or nitrification, some nitrite seems to be formed as a result of photochemical action.[60] No evidence was found of a relation between availability of nitrate and the nitrifying capacity of soils.[61] Nitrification tends to decrease with depth in soils, although the nitrate content may increase owing to gains by leaching.[62] Mineralization and nitrification of organic nitrogen proceed rapidly in peat soils leading to the accumulation of high nitrate contents.[63] Attempts have been made to develop an industrial process for the production of nitrate from ammonium salts by percolating a solution through peat.[113] In grassland soils ammonia is higher than nitrate and an equilibrium is reached between the various forms.[64, 65] Nitrification in a sandy loam is directly correlated with total soluble nitrogen and increases markedly after fertilization with ammonium sulphate.[66] In a dark chestnut soil bearing wheat ammonia accounted for

80% of the mineral nitrogen at the beginning of the vegetative period, whereas 66% was nitrate at the end of this period.[67] Inoculation of a poor Tennessee soil with a Colorado soil of high nitrifying and fixing capacity did increase the nitrogen turnover for the first year only, but the properties of the Colorado soil were not maintained for longer periods nor transmitted to the Tennessee soil.[68] A definite seasonal variation of nitrification occurs in forest soils, although correlation of the changes with those of the population of micro-organisms appears to be obscured by uptake of the nitrate formed by rapidly growing roots.[69, 70] The effect of soil type on nitrification is greater than the effect of tree cover,[71] but there is much more vigorous nitrification in the mull under hardwood stands than in the duff under hemlock or white pine.[72] Conifer seedlings grown in sand containing crude humus indicate that there is a definite relationship between rate of nitrification, development of the seedlings and growth of the associated mycorrhiza.[73]

DENITRIFICATION

There are two useful reviews of losses of nitrogen through denitrification.[74, 75] Very considerable amounts of nitrogen may be lost by this means; estimates range from 7 to 60% of the nitrogen originally present.[76–79] The losses arise as a result of the microbiological reduction of nitrate and nitrite to gaseous products.[80] Nitrite itself may react in an acid medium with amino groups or ammonia to give elementary nitrogen.[81, 82] Denitrification is inversely related to the partial pressure of the oxygen and is thus at a maximum in anaerobic conditions.[83] By the use of isotopic nitrogen it has been proved that the elementary nitrogen does in fact come from nitrate and nitrite.[84] The mass spectrometer and the infra-red spectrometer have been used to show that the products are nitrogen gas, nitric oxide and nitrous oxide,[85] the last of these being the major product under most soil conditions. The proportions of nitrous oxide and nitrogen depend on the pH value, since nitrous oxide may be reduced to nitrogen at pH values greater than 7.[86] It is suggested that soils may be the chief source of atmospheric nitrous oxide.[87, 88] An additional air pressure of 15 lb. per sq. in. had no appreciable effect on the nitrogen cycle in soil.[89] The addition of coal to the soil retarded the loss of nitrogen from both oil cake and ammonium sulphate,[90, 91] although the nitrogen of these fertilizers was rapidly lost as nitrogen gas from water-logged soils.[92] Nitrogen losses were greater in non-sterile than in sterile soils, and were also increased by exposure to light.[93, 94]

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Nitrogen Compounds as Fertilizers

A useful review[1] of earlier work on the use of artificial nitrogenous fertilizers in agriculture covers such topics as the effect of nitrogen fertilizers on the yield and

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quality of crops, relative effectiveness of different fertilizers, relation to other elements, chemical and physical effects of nitrogen fertilizers on soils, etc.

Fertilization with nitrogen compounds does give increased yields and better quality of many crops. Thus the yield of the upper leaves of tobacco is improved[2] while the nicotine content of the leaves may be greatly increased.[3] On the other hand, nitrogen fertilization increased the circumference and growth of apple trees but had no effect on the yield of fruit.[4] The largest sugar yield from sugar beet was given after a comparatively small application of nitrogen fertilizer and heavier applications increased the content of harmful or undesirable nitrogen compounds in the pressed juice.[5] The use of manure combined with artificial fertilizer gave an improved utilization of fertilizer nitrogen by crops.[6] Plant response is regarded as the only definite means of determining the fertilizer requirements of soil.[7] A close correlation has been found between the rate of accumulation of nitrates and the yield of crops.[8] Determinations of soil nitrate are thus of value for assessing the supplies of available nitrogen,[9] but it is impossible to predict the response of the soil to nitrogen fertilizers from the total soil nitrogen content.[10] The standard methods of determining the available nitrogen of fertilizers (which are based on oxidation by alkaline or neutral permanganate) are essentially empirical, and an investigation has been made of the causes of the discrepancies which frequently occur in analyses in different laboratories.[11] Studies have been made over many years of the effect of nitrogen fertilization on the nitrogen balance of the soil and it has been found that the greatest conservation of nitrogen is associated with the highest yields, although other factors, such as liming, may obscure this association.[12] In other trials annual fertilization for a period of 31 years did not increase the nitrogen content over that of unfertilized plots.[13] Nitrification is often checked for a time after fertilization.[14] Conversion of fertilizer nitrogen to organic forms unavailable to plants is much greater in cropped than in fallow soils.[15] The granule size of mixed fertilizers had no effect on the rate of transfer of inorganic nitrogen into the soil, although the transfer of organic nitrogen was slower from larger granules.[16]

The relative effectiveness of different nitrogen fertilizers for crop production has been reviewed.[17] Ammonium sulphate may still be an effective fertilizer in soils which contain large amounts of ammonium nitrogen,[18] while in other cases the yearly yield increases may decline with repeated application of this fertilizer.[19] It is very likely that both these effects may be due to the changes in the soil pH value produced by ammonium sulphate. This salt has been found to cause increases in available soil nitrogen in tropical soils for 3–4 months[20] and in temperate soils for 2 months.[21] The higher was the nitrate content of the soil at seeding time the less was the response to fertilization with ammonium sulphate.[22] Considerable losses of ammonia may occur, particularly in soils containing calcium carbonate,[23] the loss ranging from 50–60% at pH value 8 to 5% at pH 6.[24] In Indian soils retention and absorption of nitrogen is higher from ammonium chloride than from ammonium sulphate.[25] The effect of sodium nitrate on soils is the less the higher is the nitrifying power.[26] Leaching losses of sodium nitrate were not found to be serious in a clay soil; they depended to some extent on the crop, timothy being most effective in conserving the soil nitrogen.[27] Field tests using a variety of crops show that in general there is no significant difference between different sources of nitrogen when used as fertilizers.[28–30] Grass appears to take up nitrogen more rapidly from nitrates than from ammonium salts but the difference is not great.[31] Slightly higher recoveries of nitrogen were obtained from nitrate than from ammonium fertilizers[32] and, when a mixture of the two was used, more than 60% of the fertilizer nitrogen was converted to protein by herbage.[33] The relative values of nitrate and ammonium salts depend on the pH value of the soil, both being approximately equal in soils of pH 5·5–6·5, but the nitrate is superior at both lower and higher pH.[34] Ammonium nitrate gives a slightly but definitely higher yield of potatoes than either ammonium sulphate or sodium nitrate,[60] but there is danger of scorching of foliage.[61] Anhydrous ammonia has been applied by injection in sandy soils, and although the ammonia tends to be concentrated in narrow zones retention is variable.[62] The continued use of ammonium

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sulphate reduces the soil pH value until plant growth is adversely affected.[35] For this reason lime is usually recommended to be used with this fertilizer.[36, 37] Some soils may, however, give better results with acidic or neutral than with alkaline fertilizers.[38] Urea and calcium cyanamide act physiologically alkaline in soils but later tend to become slightly acid; they are most effective at pH value 7.[39] Most nitrogen fertilizers result in an increase of soil ammonia for a few weeks after application, this ammonia then decreasing as the soil nitrate increases. These changes are reflected in changes in soil pH value.[40, 41] Fertilization with calcium cyanamide may lead to higher concentrations of soil nitrates than fertilization with sodium nitrate.[42, 43] The rate of application and depth of placement of the cyanamide appear to be important factors in determining the nitrogen transformation.[44] The soil type is also important since under some conditions calcium cyanamide may be hydrolysed to urea, in others to dicyanodiamide.[45] After 14 days no difference was detected between the inorganic nitrogen content of soils treated with ammonium sulphate or calcium cyanamide.[63] Ammonium sulphate was found to be the most rapidly and most completely nitrified of a series of fertilizers, but Peruvian guano is nitrified almost as fast.[46] Ammonium sulphate applied in November during a mild winter was 60% converted to nitrate in two months and completely in six months, by which time only 36% of the nitrate remained in the soil.[64] Many unusual nitrogen compounds have been tested as fertilizers, such as formamide and other simple aliphatic amides,[47] urea–formaldehyde reaction products,[48] nitric acid[49] and liquid nitrogen dioxide.[50]

Both assimilable phosphate[51, 52] and potassium[53] increase the utilization of nitrogen by plants, while ammonium sulphate and other nitrogen fertilizers (which decrease the soil pH value) also increase the uptake of phosphate by plants.[54, 55] Because of this interaction fertilizers are usually compounded to contain a definite ratio of available nitrogen, phosphate and potassium. It has been claimed that each particular crop has an optimum ratio of the three nutrients,[56–58] but more carefully controlled tests indicate that wide variation of the mineral salt ratios may not produce significant differences in the yields of cereals.[59]

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Occurrence of Nitrogen in Plants

It is difficult to give figures which express the normal nitrogen content of plants since this is affected by many factors. Determinations of the sulphur, phosphorus and nitrogen contents of many common vegetables and crops grown on the same soil under the same conditions show that plants do vary widely in their normal nitrogen content.[1] The fruit and seeds of a mature apple tree take up from the soil 0·33 lb. per year of nitrogen as against 0·5 lb. per year permanently incorporated in new wood and root growth and 0·67 lb. per year taken up by the leaves and flowers which fail to set; the last quantity of nitrogen is returned to the soil at leaf fall.[2] The effect of weather is regarded as more important than that of variety in determining the nitrogen content of peach flower buds,[3] but significant differences in the nitrogen content of orange leaves are attributed to the effect of different rootstock.[4] The nitrogen content of component parts of the maize kernel in decreasing order is: germ, endosperm, hull and tip cap. Selecting the variety of maize for high or low protein affects the nitrogen content of the endosperm much more than that of the germ. The nitrogen contents of all parts increases with fertilization of the soil.[5] The total yield, roots plus tops, of different varieties of sugar beet is found to be inversely proportional to their nitrogen content.[6]

Nitrogen Deficiency in Plants

The visual symptoms of nitrogen deficiency in many common crop plants have been illustrated by colour plates in a guide to diagnosis.[7] The effects of deficient supplies of nitrogen have been studied on most economic plants[8] and particularly on fruit trees.[9, 10] Deficiency may cause increased susceptibility of peach trees to cold injury,[11] apple trees may become withered and eventually die,[12] peas become yellow and die, whereas oats do complete their life cycle although growth is retarded.[13] It has been shown that nitrogen deficiencies in antirrhinum may increase the rate of mutation as a result of the disturbances of metabolism.[14] Leaf coloration in apple leaves appears to be associated with a nitrogen content of about 1·9–2·1%.[15] An excessive supply of nitrogen has been found to result in poor growth in sweet peas[16] and to cause the disease brusone in rice.[17] Tip burn occurs in sugar beet when grown with abundance of nitrogen under low light intensities,[18] while peas develop necrosis at low pH values with ammonium sulphate as the nitrogen source.[13] In some cases these effects seem to be due to a direct toxicity by ammonia,[19] but it is known that excess supplies of nitrogen can lead to boron deficiency in plants.[20] The interdependence of mineral nutrition is also shown by the fact that all forms of nitrogen increase in the plant in lime-induced chlorosis of lupines.[21]

Absorption of Nitrogen by Plants

The general nitrogen nutrition of plants has recently been reviewed.[22, 23] Sugar cane may absorb sufficient nitrogen at an early stage of development to last for the remainder of the life of the plant, without further uptake.[24] High-yielding varieties of sugar beet have a lower nitrogen content than low-yielding varieties, so that the total amount of nitrogen removed from the soil tends to be constant irrespective of the variety.[25] The distribution of Sitka spruce and western hemlock seedlings in Alaska is found to reflect the distribution of nitrate in the soil, the percentage of spruce increasing with increasing nitrate content up to a maximum of 50 p.p.m.[26] Although absorption of nitrogen by barley is independent of the time of sowing, delaying the date of sowing reduces the amount of dry solid material formed by the plant so that the nitrogen content appears to rise.[27] The water requirement necessary to form a given weight of cereal varies inversely with the available nitrogen.[28] The nitrogen content of wheat or rye is, however, reduced by drought while that of grapes is higher in humid years.[30] When the supply of nitrogen is liberal the degree of xeromorphism declines while the total surface, the degree of succulence, water content and size of the epidermal cells all increase.[31] Similarly the viscosity of the protoplasm of cereals increases together with the drought resistance as the nitrogen supply falls.[32]

Many plants respond well to foliar feeding by spraying the foliage with an aqueous solution of ammonium nitrate or sulphate.[33] The ammonium ion is rapidly translocated to more rapidly metabolizing tissues either before or after conversion to organic nitrogen compounds.[34] There has been some speculation as to whether some plants can absorb nitrogen through the roots in the form of ammonia.[35] The question has been decisively settled by the use of isotopic nitrogen which has shown that not only *Chlorella*[87,88] but also tomato[89] and rice[90] absorb, translocate and utilize ammonium ion very rapidly, the process being coupled to the metabolism of carbohydrate. Sugar beet, however, responds to nitrate fertilization in preference to that by ammonium salts, and the leaves of plants cultivated with ammonium fertilizers consume increased oxygen.[91] This plant appears to be devoid of the enzyme nitrate reductase.[92] Rice produces less yield and more sterile heads when supplied with ammonia in nutrient solution than with nitrate.[36] The use of isotopic nitrogen indicates the possibility of fixation of atmospheric nitrogen through the aerial parts of barley plants, though direct nitrogen exchange is an alternative explanation.[37] Nitrogen fixation has been demonstrated in detached non-legume root nodules.[38] Many aspects of the nitrogen economy of grass–legume association have been reviewed.[39] The reduction in nodule formation in many legumes which occurs in the presence of high concentrations of soil nitrogen is ascribed to a lowering of the available carbohydrate supply.[40, 41] Nitrogen fixation reaches a maximum when the soil nitrogen lies within a certain range; with little or no available nitrogen legumes die before the development of nodules, while if the nitrogen supply is too high, little or no fixation occurs.[42] The mycorrhizal fungi associated with conifers may supply considerable nitrogen to the plant,[43] while mycorrhizal development is retarded with high levels of nitrogen supply.[44] It has been claimed that gaseous nitrogen may be lost by cultures of *Chlorella*,[45] but this was confirmed only when ammonium nitrate was the source of nitrogen, no loss being found with other nitrogenous salts or with higher plants.[46]

The absorption of nitrogen is also dependent on the relative abundance of other mineral elements. Nitrate is the dominant anion in plants and thus plants with a high total cation content also tend to have a high nitrogen content. Cationic nitrogen as in ammonium salts conversely tends to suppress the total cation content and to promote increased absorption of other anions.[47] There is a highly significant correlation between the nitrogen content of apple leaves and the available soil potash,[48] while an optimum ratio of potash to nitrogen is necessary for maximum assimilation in cereals.[49, 50] Potassium appears to have a greater influence on the assimilation of ammonia than on its absorption, and the increased absorption of ammonium ions by beet embryos in the presence of potassium chloride is attributed to the chloride anion.[51] Reduction of the potash or magnesium available to oats reduces the content of insoluble nitrogen, whereas reduction of calcium reduces the total nitrogen content.[52] Liming the soil does tend to increase the uptake of nitrogen by plants except by sweet clover.[53] The effect of sodium chloride in increasing the absorption of nitrogen by bean plants is ascribed to the direct effect of the sodium salt on the permeability of the plant cell walls.[54] Increasing the osmotic pressure of the soil solution by the addition of sodium chloride or sulphate appears to cause more efficient assimilation of nitrogen.[55] Deficiency of iron increases protein and total nitrogen in corn plants,[56] while the nitrogen supply appears to control the copper content of tung leaves[57] and of protein sulphur in a number of species of plants.[58, 59]

Increase in the supply of nitrogen increases the formation of chlorophyll with a resultant increase in nitrogen assimilation.[60, 61] No anthocyanin pigments appear to be produced when the nitrogen supply is ample, but suppression of this supply causes rapid formation of anthocyanins in the leaves, followed by early death.[62] Abundance of available nitrogen in the soil also appears to control the formation of carotene in grasses and cereals,[63, 64] nicotine and other nitrogen bases in tobacco,[65, 66] the alkaloid contents of *Lobelia inflata*,[67] the arbutin content of *Bergenia delavayi*[67] and the essential oils of *Mentha piperita*.[68] The optimum yield of rubber by kok-saghyz requires moderate nitrogen nutrition during the early stages of growth, followed by an increased nutrition during the later stages.[69, 70] A variety of wheat was completely resistant to the stem rust, *Puccinia*, when supplied with ammonium salts as a nitrogen source but completely susceptible when nitrate was used. These results, however, did not appear to obtain in the field.[71] Studies of the cytogenetic effects produced by thermal neutrons on *Tradescantia* microspores indicate that much of the ionization dose is due to neutron capture by nitrogen atoms in the plant tissues with subsequent emission of protons.[72] Nitrous oxide at certain pressures and concentrations has been found to cause mitotic effects in the roots of *Allium cepa* bulbs.[73] Nitrates do not appear to accumulate in the leaves of plants exposed to concentrations of nitrous gases sufficient to cause leaf burn.[74] Nitrogen dioxide is toxic to plants at concentrations of the order of 1 in 10^4 by volume.[75]

Movement of carbohydrate and nitrogen can take place in opposite directions through the same sieve tubes in leaves.[76] In the earlier stages of growth nitrogen may be absorbed faster than it is assimilated. Large amounts of nitrogen are converted to substances other than protein.[77] A rapid exchange of nitrogen in leaf protein occurs when isotopic nitrogen in the form of ammonium chloride is supplied to buckwheat or tobacco, suggesting that this protein is in equilibrium with amino acids or simple nitrogen compounds in the leaf.[78] A decrease in all forms of nitrogen is found in successive leaves from base to apex of the rice plant.[79] Nitrogen and phosphate have opposing effects on the levels of peactase and protease activities in tobacco.[80] During vernalization of cabbage the total nitrogen and the protein contents increase greatly.[81] Transamination reactions are very active in plant tissues without equilibration with a metabolic pool of ammonium ions.[82] After immersion of red beet in a solution of ammonium nitrate labelled with ^{15}N in the cation, glutamine was isolated with 23·3 atom-% excess of ^{15}N in the amide group but only 3·42 atom-% excess in the α-amino group.[83] Nitrogen starvation reduces the respiration rate of *Lemna*, the effect being opposed by illumination.[84] Conversely at high levels of supplementary illumination soluble nitrogen is decreased in the tissues of asters.[85] Spraying beets with 2,4-D solutions greatly increased the nitrogen content of the roots, particularly in the small tubers which are formed.[86] The use of isotopically labelled ammonium salts in the study of the assimilation of ammoniun ion has begun to throw some light on the process. Thus, nitrogen compounds are highest in the embryo of growing rice seeds,[93] and the most abundant compounds are glutamine and aspartine together with the free acids, although there may be considerable synthesis of amides, particularly in the roots.[89] The nitrogen of these amines or amides then undergoes exchange reactions to synthesize other amino acids and ultimately proteins.[90, 94–96] Almost all the protein and the pyrrole rings of chlorophyll appear to be renewed every 100 hours in young green tissue.[97] Alanine, tryptophane and lysine occur in higher concentrations in plants treated with cyanamide than in those treated with calcium nitrate.[98] A number of plant juices appear to be able to reduce nitrate to nitrite,[99] although potato juice retards the reduction caused by ascorbic acid.[100] Nitrites are also produced in the rhizosphere around actively respiring roots of crop plants.[101] The juice of the lilac reduces nitrite to hydroxylamine.[102] Hydroxylamine has been shown to stimulate the fixation of carbon dioxide during photosynthesis by algæ.[103]

Free ammonia may be present in plant tissues, and the concentration which a plant may tolerate appears to be dependent on the pH of the cell sap as well as on the nutritional status of the plant.[104] Detoxification of ammonia is by means of salt formation when the pH value is below 5·5 and by amide formation to glutamine or aspartine at higher pH values.[105] Free ammonia is produced in many plant tissues on drying; it arises not from glutamine but from some unknown precursor.[106] Ammonia is formed in germinating garden beet seeds by bacterial reduction of nitrates, and the ammonia is an inhibitor of germination.[107] Treatment of barley roots with 0·001 p.p.m. of sodium azide stimulated the uptake of phosphate ion, whereas 10 p.p.m. inhibited uptake.[108] Sodium azide was the most effective compound of a series tested for control of black root rot of tobacco in greenhouses but as regarded as too dangerous for general use.[109]

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NITROGEN COMPOUNDS AND INVERTEBRATES

The metabolism of ammonia in invertebrates has been reviewed[1]

(*a*) Insects

A number of species of *Anopheles* develop normally in breeding waters containing ammonia concentrations of 0·1–0·4 mg./l., while *Culex pipiens* is found at concentrations up to 5 mg./l. Two species which normally inhabit tree cavities, *Anopheles nigripes* and *Aedes ornatus*, have been found to thrive in ammonia concentrations up to 30 mg./l.[2] Many insect larvæ excrete most of their nitrogen as ammonia, and the concentration in the hindgut may rise to 136 mg./100 ml. in *Sialis lutaria* larvæ[3] and exceed 500 mg./100 ml. in the larvæ of *Lucillia cuprina*.[4] It has been claimed that micro-organisms living in symbiosis with insects are capable of fixing atmospheric nitrogen,[5] but experimental results appear to reject this claim.[6] Large quantities of ammonium bicarbonate are excreted by larvæ of the blowfly, *Phormia regina*.[7] The housefly is attracted to ammonia solutions with a concentration of 0·012% by volume and is repelled by solutions of 0·03%, the females being more strongly attracted than males.[8] Ammonia is not attractive to female *Aedes ægypti*,[9] but a solution of ammonium chloride is a non-orienting repellant when applied to the labella.[10] Ammonium carbonate has been used as a trap to determine the emergence of the cherry fruit fly, *Rhagoletis cingulata*,[11] and also to control houseflies.[12]

Treatment of silkworms by solutions of potassium nitrite or hydroxylamine resulted in cytological changes such as enlarged nuclei, aggregation of chromatin threads and amitosis,[13] and descendants of these silkworms showed inherited abnormalities.[14] Although 1% ammonia solution has a high toxicity for *Drosophila melanogaster*, survivors have a greatly increased mutation rate.[15, 16] Sodium azide at a concentration of 0·003 M. also increased the frequency of sex-linked lethals after *X*-irradiation.[17] Hydroxylamine or potassium nitrite fed or injected into silkworms increased the activity of certain enzymes, notably deoxyribonuclease and ribonuclease.[18, 19] Sodium azide decreases the luminescence of *Cypridina* by direct reaction with luciferin but has little effect on the luciferase.[20] Sodium nitrite has been tested with some success as an insecticide.[21]

Fumigation of citrus fruit by a mixture of ethylene dibromide and nitrogen trichloride killed 93·5–96·4% of the larvæ of *Ceratitis capitata*, whereas ethylene dibromide alone at the same concentration–time product killed only 75%. There was some damage to grapefruit but not to oranges.[22] It has been suggested that the susceptibility of *Drosophila* to hydrogen cyanide is measured more accurately by calculating the percentage which recover in a definite time rather than by assessing the percentage mortality.[23] Nitrous oxide has no effect on honey bees unless the oxygen content is below 2%. Fumes from a smoker containing cardboard treated with ammonium nitrate were particularly toxic and had a high anæsthetizing capacity.[24] The toxic partial pressure to *Sitophilus granarius* in the presence of air at 1 atm. was for nitrogen 340 atm., and for nitrous oxide 14·5 atm. with a 5 hr. exposure period.[25] Exposure to 80% nitrous oxide prevents the spider *Zilla notata* from spinning a web. The spider appears to undergo an excitatory phase before anæsthesia.[26]

(*b*) Helminths

Between 40 and 60% of the total nitrogen excreted by *Ascaris suis* and *Monieza expansa* is ammonia.[27] The mechanism of formation of ammonia by *Planaria* and certain trematodes and cestodes is obscure since the usual deaminating enzymes cannot be identified.[28] Ammonia inhibited hatching of cysts of *Heterodera rostochiensis*, the effect probably being due to a high pH value, since strong ammonium salts such as the sulphate, chloride or nitrate were without effect.[29] Ammonia is toxic to the bursate nematodes of horse and sheep, and the lethal action of bacteria on *Eustrongylides* larvæ is ascribed to the formation of ammonia by these bacteria.[31] The numbers of nematodes of all types in soil were drastically reduced by treatment of the soil with anhydrous ammonia.[32] A number of organic azides applied to soil gave effective control of several species of plant parasitic nematodes, the effect being ascribed to the liberation of hydrazoic acid in moist soil.[33]

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NITROGEN COMPOUNDS AND MARINE AND FRESHWATER ORGANISMS

The nitrogen economy of freshwater lakes and rivers has been widely studied.[1, 2] The nitrogen and ammonia content of rivers often shows a diurnal variation, being at a maximum at night.[3, 4] Many evolved and mature lakes have in the bottom mud large nitrogen reserves which must come either from the activity of some nitrogen-fixing organism or from deposits of plankton.[5] The mud of many lakes has been examined, and often the nitrogen content is closely correlated with the population of micro-organisms.[6] The nitrogen content of the mud of 46 Russian lakes varied from 0·23% in highly mineralized lakes to 4·23% in high plankton lakes. The carbon to nitrogen ratio varies from 7·43 to 26·3.[7] Lakes may of course receive considerable additions of nitrogen from inflowing waters, but often as much as 50% of this incremental nitrogen is rapidly converted to the organic form by algæ.[8] The nitrogen increase may thus show a marked dependence on the season; it is highest in August in Russian lakes.[9] A brackish lagoon had a very low ammonia content and a high albuminoid nitrogen content, probably derived from decaying plankton. Nitrite could be detected only in winter.[10] Attempts have been made to correlate the growth of different species of diatoms and algæ with the concentrations of different forms of nitrogen. An inverse relation was observed between the abundance of diatoms and concentration of nitrate, but there was no correlation with ammonia. Apart from this case there seems to be little correlation, although some 140 different species of algæ were identified.[11, 12] Green algæ have been claimed to fix nitrogen in fresh water.[13]

Much attention has also been devoted to the nitrogen cycle in the sea.[14] Formation of nitrite from ammonia is inhibited at temperatures below 5°C. No evidence has been found for fixation of atmospheric nitrogen in sea water.[15] The organic nitrogen of sediments may be regenerated as ammonia, which becomes converted to nitrate.[16] Determination of the nitrogen content of sea water has been found to be a more accurate measure of the biological activity than determination of the oxygen content.[17] The carbon: nitrogen ratio of surface waters is usually lower than that of nearby deep water.[18, 19] The nitrogen: phosphate ratio varies with depth, and the surface value is usually between 8·8 and 14 in the Philippines[20] and about 20 in British coastal waters.[21, 22] The ratio is constant and independent of the season in deep waters, whereas in surface layers the ratio varies with the influx of coastal waters, rate of growth of plankton, etc.[23] The relationship between nitrogen and phosphate contents of sea water and marine organisms has been discussed.[24, 25] Both ammonia and nitrate are utilized by freshwater algæ and bacteria. Gaseous nitrogen is evolved by the cultures.[29] Ammonium ion enters cells of *Valonia* as undissociated ammonia until the concentration inside the cell sap is over 40 times that of the surrounding sea water.[30] The ammonia-nitrogen content of marine animals varies widely, thus the hæmolymph of molluscs contains 0·50–0·33 mg. %,[34] the blood of crustacea may contain 0·295–1·8 mg. %,[33–35] the cuttlefish *Sepia* may have 3·85 mg. % in the blood, while the high value of 12·17 mg. % has been found in the tunicate *Ascidiella*.[34] Sterile sea urchin eggs continuously produce ammonia, but after fertilization ammonia ceases to be produced and is utilized for synthetic purposes.[36, 37] Isotopic studies show that incorporation of ammonia nitrogen into pyrimidines and purines increases after fertilization.[38] During the early stages of development nitrogen metabolism consists mainly of transamination reactions, but later incorporation of ammonia into amino acids becomes important.[39] Electrical stimulation of the non-medullated nerve of *Anodonta* resulted in a 370% increase of ammonia production.[40] Nitrous oxide caused a definite delay in the first cleavage of the eggs of *Arbacia punctulata* at pressures of 2·3 atm. owing to narcosis, whereas nitrogen gave no signs of narcosis at pressures of 61 atm.[26] By means of isotopic nitrogen it has been shown that trimethylamine penetrates into the interior of the axon of squid nerves, while acetylcholine does not; this indicates that the site of action of acetylcholine is limited to the synapse.[27] Marine invertebrates excrete most of their nitrogen as ammonia, as to the larvæ and embryos of all animals living under aquatic conditions. Ammonia excretion disappears with increasing complexity of the organism and is replaced by urea excretion.[41] The change from ammonia to urea excretion occurs during the metamorphosis of amphibia amongst those species ultimately intended for a terrestrial environment.[42] Approximately 6–10 times as much nitrogen (largely urea and ammonia) is excreted by the gills of freshwater carp as by the kidneys.[43] The form in which nitrogen is excreted by chelonian reptiles appears to vary with the habitat. Thus aquatic species excrete both ammonia and

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urea in approximately equal quantities. Species living in marshy ground excrete very little ammonia and more urea while terrestrial species living in dry habitats excrete 60% of their nitrogen as uric acid.[28] Ammonium chloride and sulphate are more toxic to trout in hard water of pH 6·5–7·8 than in distilled water of pH 5·3–6·3, the limiting concentration being about 100 p.p.m. of ammonia.[44] Treatment of the eggs of a number of marine animals by low concentrations of sodium azide results in the development of malformed larvæ.[45–47]

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NITROGEN COMPOUNDS AND VERTEBRATES

Nitrogen plays a most important rôle in the metabolism of vertebrates and it is essential for health that the intake and excretion of nitrogen compounds shall be correctly balanced. Recent reviews exist on the general topics of nitrogen balance,[1] on autoregulation of nitrogen metabolism,[2] on the synthesis and degradation of proteins[3] and on the use in biochemistry and physiology of the heavy isotope, ^{15}N.[4–6]

Metabolism of Nitrogen Compounds

The techniques of determining the percentage of the ^{15}N isotope in proteins and amino acids have been described.[7, 8] When rats are fed on a diet containing labelled ammonium citrate, a small part of the ammonium ion is utilized for amino acid and creatine synthesis.[7, 9] When men are given a single oral dose of ^{15}N-labelled glycine, 30% is excreted during the first 24 hours, and 40% by the end of 48 hours, the remainder being incorporated in a metabolic nitrogen pool. It is calculated that the rate of protein synthesis in the human being is 0·20 and in the rat 1·0 g. of N per kg. of body wt. per day.[10] There is also some evidence of direct exchange of amino groups or even of glycine.[11] The transfer of isotopic nitrogen from glycine to the α and δ amino groups of ornithine appears to require a transamination mechanism followed by an intramolecular shift.[12] Ammonia itself is not an intermediate in transamination.[13] Unlike amino acids the purines and pyrimidines of the diet are immediately metabolized to their end-product and are synthesized as required from other nitrogen compounds.[14] In rats and pigeons ammonia nitrogen rapidly exchanges with the nitrogen of purines and pyrimidines of nucleic acids, but to a much smaller extent with creatine or adenylic acid. In birds there is some evidence that the former pathway is the normal metabolic route for the conversion of ammonia to uric acid (in which form birds excrete the bulk of their nitrogen).[15] Adenine fed to rats is partly converted to guanine before synthesis into nucleic acids.[16] Amino acids have long been divided into essential and non-essential, i.e., those that cannot and those that can be synthesized by the body,[17] and omission of any essential amino acid markedly affects the nitrogen balance of the organism.[18] Careful studies indicate that less than 2·55 g. of nitrogen per day is required by young men for the synthesis of non-essential amino acids.[19] About 1 g. of nitrogen per day is required by adults for normal growth, that is mainly of the skin and hair.[20]

The kinetics of excretion of isotopic nitrogen have been analysed mathematically. Results indicate that during immobilization there is reduced synthesis of proteins while breakdown remains unchanged, so that there is more nitrogen lost from the body than normally.[21] Nitrogen excretion increases with increasing altitude, reaching a maximum at 4000 m. There is concurrently a loss of body weight, suggesting that nitrogen metabolism is inhibited at low pressures.[22, 23] On fasting or after sudden restriction of the protein level of the diet, there is a lag in the adjustment of the urinary nitrogen to a lower level, which is ascribed to increased breakdown of liver proteins.[24] The mechanism of the increased retention of nitrogen after kidney damage or disease has been thoroughly discussed.[25] The nitrogen content of the fæces shows little change with variation of diet.[26] Normal sweating may result in nitrogen losses of about 0·36–0·38 g. per day, which is about 2·7% of the total daily nitrogen excretion, but the nitrogen content of sweat increases in profuse sweating until the loss may reach 22·7% of the total excretion.[20, 27]

About 24% of the food nitrogen of pigs could be replaced by ammonium citrate with no adverse effects,[28, 29] while rats and men excreted the salt almost quantitatively, unless on a low protein diet when it was utilized almost as effectively as glycine.[30] Conversion of inorganic ammonium salts to amino acids and proteins

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under the action of micro-organisms occurs in the cow rumen.[31] Ammonia can be detected in the respired air of rats which have been fed with ammonium salts.[32] Injection of ammonia into the blood stream increases the amide nitrogen content of the blood,[33] while inhalation of ammonia causes a lowering of blood pressure and an increase in non-protein nitrogen in the blood, although the pH value does not change.[34]

Physiological Effects of Nitrogen Gas

Much attention has been paid to the problem of decompression to remove excess of nitrogen absorbed by divers. The elimination of nitrogen seems to be more rapid when oxygen is breathed at a pressure corresponding to a depth about half the working-depth.[35, 36] Bubbles were formed on decompression in many mammalian tissues even in the absence of gas nuclei, but not in living unicellular protozoa.[37] The curve of nitrogen elimination during oxygen breathing shows three different rates in the ratio 100:10:1. The first is believed to be that due to release from highly perfused tissues, the second from muscles and the third from fat deposits.[38] This is also borne out by studies of the rate of saturation of various tissues. At 3 atm. pressure of nitrogen the bone marrow becomes 25% saturated in 1 hr., 60% in 4 hr. and 90% in 8 hr.[39] In dry, uncomplicated pneumothorax there is equilibrium with lowered oxygen and raised nitrogen partial pressures, an effect difficult to explain by differential permeabilities through the lung wall.[40] The high partial pressure of nitrogen in intestinal flatus is believed to be due to the high blood-nitrogen content which reduces absorption of this gas through the wall of the colon.[41] A pneumoperitoneum of 500 ml. of nitrogen was absorbed almost linearly for the first 8 days at a rate of 30 ml. per day, complete absorption occurring at 23 days.[42] At very high pressures nitrogen had a narcotic effect, the time for narcosis of mice decreasing as the pressure increased from 1·5 hr. at 10 atm. to 40 min. at 54 atm.[43, 44] In this effect, which appears to be due to removal of oxygen from the nervous tissue, the action potential of nerves is reduced while the excitability remains unchanged.[45] A modified Haldane gas analyser has been found useful for studying the rate of elimination of nitrogen from body tissues.[46]

Ammonia in Vertebrates

The chief difficulty in the determination of ammonia in biological fluids, apart from the very low concentrations encountered, results from the presence of urea which readily decomposes to yield ammonia. Accurate methods based on careful aeration techniques and use of the Nessler reaction have been developed.[164–166] Normal human gastric juice contains 2–9·8 mg./100 ml. of ammonia,[167–169] pancreatic juice 0·013–0·18 mg./100 ml.,[170] sweat 5–35 mg./100 ml.[171] The ammonia content of human blood is much lower and is also subject to wide variation, part of which may be ascribed to differences in analytical technique. Typical values are (mg./100 ml.) 0·03–0·016,[172] 0·003,[173] 0·02–0·42,[174] 0·01–0·075 (mean 0·025),[175] 0·047.[176] The blood of dogs contains 0·01–0·02 mg./ml.[177] The mean ammonia content of 122 urines from 16 persons was 98 mg./100 ml.[178] The blood ammonia content is readily changed by abnormal physiological and by pathological conditions. Thus it is increased by hyperventilation,[179] by exertion at high altitudes,[180] by obstruction of the trachea, lowering of atmospheric pressure and reduction of oxygen tension,[181] and by acidosis following the injection of ammonium chloride.[182] The blood ammonia is not changed during cirrhosis of the liver or diabetic acidosis but is increased in pulmonary tuberculosis.[176] Very high values have been reported 1–3 hr. before the onset of epileptic seizures,[183] but this increase is not invariable and cannot therefore be the cause of the seizure.[184] The ammonia content of the saliva varies widely and probably arises from hydrolysis of urea.[185, 186] If ammonia is determined by aeration for 10 minutes of freshly-drawn blood, a low value is obtained. This value increases as the blood is kept for 30 minutes, after which little further change occurs for 3–4 hr.[172] It has been suggested that blood contains no preformed ammonia but that this arises from some precursor.[173] It has been shown that the ammonia of the blood is not produced by any particular organ such as the kidneys but is a general tissue phenomenon.[187] There is a great increase in blood ammonia at death.[188] Ingestion of ammonium salts results in an increase in the blood amide nitrogen which is rapidly excreted by the kidneys and it is probable that this represents a detoxification mechanism.[189, 190] The increase in blood ammonia immediately after collection of the sample arises by deamination of adenosine or adenylic acid while the later increase is possibly due to breakdown of adenosine triphosphate.[191] Ammonia is produced by muscle during contraction,[192] the amount being directly proportional to the number of contractions, about 1 mol. of ammonia being produced for 14 mols. of lactic acid.[193] This ammonia arises from the deamination of adenylic acid to inosinic acid during contraction,[194] and the formation is inhibited by magnesium ions.[195] Adenosine triphosphate itself does not appear to be readily deaminated, but part of the adenylic acid formed after the transfer of high-energy phosphate to phosphagen may escape resynthesis and be deaminated.[196, 197] There also appears to be a second ammonia-producing substance present in muscle.[198] Nerve fibre produces ammonia during excitation to a much greater extent than does muscle.[199–201] The ammonia content of the dark-adapted frog or cow retina increases greatly on exposure to light,[202–203] the mechanism once again being the deamination of adenylic acid.[204] Although the ammonia content and the pH value of urine tend to vary inversely, the product of ammonia nitrogen and pH is not always constant,[205] and more complex relationships between these two quantities have been sought.[206] Urinary ammonia is decreased after forced rapid breathing[207] and during fatigue,[208] but increases after muscular exertion.[209] There is a greater excretion of ammonia at night than during the day.[210] Administration of ammonium chloride resulted in an increased excretion of ammonia without increase in the total nitrogen content of the urine,[211] but the ratio of ammonia nitrogen to total nitrogen of the urine appears to have no relation to the protein composition of the diet.[212, 213] The ammonia excreted in the urine is greater than can be accounted for by the blood ammonia which has passed through the kidney, thus providing evidence of the origin of ammonia in that organ.[213–215] Synthesis of ammonia by the kidney is at a minimum during acidosis and is depressed by quinine and phloridzin.[216] Excretion of ammonia does not involve active transport but passive diffusion.[217]

Ammonia acts as an irritant mainly on the upper respiratory tract. A concentration of 200 p.p.m. is regarded as dangerous to breathe for 1 hr.[218] Guinea pigs tolerate long exposure to 1·5 g./l. but develop catarrhal pneumonia with 2·5 g./l. Rabbits are, however, more resistant.[219] Administration of ammonium chloride produces an acidosis in the blood which in turn evokes the synthesis of excess blood ammonia to neutralize the acid. There is a time lag of 5–7 days both in the development and in the cessation of this synthesis.[220] The cerebro-spinal fluid, however, becomes alkaline after the oral ingestion of ammonium chloride probably because of the more rapid diffusion of ammonium ion.[221] Ammonium chloride appears to have a marked stimulatory effect on the respiratory centre[222] and increases both the red cell count and the oxygen capacity of dogs exposed to low barometric pressures.[223] It has successfully prevented the death of rabbits from sudden decompression to a low atmospheric pressure.[224] Ammonium bicarbonate has a marked healing effect on purulent wounds and stimulates the growth of tissues.[225–227] Ammonium ion is utilized by liver to form glutamic acid[228] and may have a marked ketogenic effect if the TCA cycle is blocked.[229]

Nitrites in Vertebrates

A delicate colorimetric method has been developed for the determination of nitrite in blood.[230, 231] The normal mean nitrite content of the blood of dog, steer and man is 9·5 μg./100 ml.[232] Oral administration of sublethal doses of sodium nitrite over a long period of time produces degenerative lesions in the main organs.[233] Sodium nitrite increases both the volume and the acidity of gastric secretion,[234] paralyses striated muscle in frogs[235] and has a pronounced vaso-dilatory action.[236–237] Injection of sodium nitrite is an effective antidote to poisoning by cyanide,[238–240] by hydrogen sulphide[239] and by fluoride.[239] Nitrite combines with the hæmoferrin of methæmoglobin to form an undissociated compound which diminishes the oxidising activity of the blood.[241]

Azides in Vertebrates

Injection of non-lethal doses of sodium azide conferred considerable protection against the lethal action of body *X*-irradiation.[241–244] Azide completely inhibits the oxidation of cytochrome *c* by cytochrome oxidase,[245] a complex between enzyme and inhibitor being formed.[246]

Anæsthesia by Nitrous Oxide

The use of nitrous oxide for anæsthesia was discovered by Horace Wells in 1844,[47–49] and its use has been thoroughly reviewed.[50] Nitrous oxide finds considerable application in gynæcology, since it is least likely to irritate the lungs[51] and gives protection of the circulation with few after-effects.[52] Tests have been designed for the purity and in particular the acidity of the gas.[53, 54] The range between the minimal anæsthetic and minimal lethal concentrations is greater than for any other common anæsthetic gas.[55] Nitrous oxide is commonly used in admixture with other agents such as oxygen,[56] acetylene[56, 57] and ether,[58] or in conjunction with other drugs such as sodium pentothal[59] and avertin.[60] Each mixture is claimed to have certain specific advantages. Complex apparatus has been designed to permit the administration of the gas in a closed system with absorption of the expired carbon dioxide.[61, 62] The concentration range of nitrous oxide in oxygen or air which gave the maximum degree of analgesia while still retaining the co-operation of the subject is 35–40%.[63] Determinations of the concentration of nitrous oxide in the blood have been made by means of the mass spectrometer,[64] by infra-red spectroscopy[65] and with a specialized apparatus using the principle of infra-red absorption which simultaneously measures nitrous oxide and carbon dioxide.[66]

The rate of uptake of nitrous oxide has been measured in man during surgical anæsthesia. After 90 min. inhalation of an 80% N_2O–20% O_2 mixture, the body still absorbs 100 ml. per min. of nitrous oxide, the rate of absorption during the first 2 hr. of anæsthesia being about 30 times the rate of elimination.[67] Considerable amounts of nitrous oxide were found to diffuse through the skin of patients during anæsthesia. The low concentrations diffusing were estimated by a chemical method.[68] The Bunsen coefficient of the solubility of nitrous oxide in blood is 0·415,[69] 0·412.[70] The solubility in brain has also been measured. During anæsthesia the blood concentration of nitrous oxide is approximately 25 vol.-%, but anæsthesia depends upon the concentration of oxygen[71–73] and cannot be produced unless the oxygen partial pressure is below that occurring in air.[74] For sustained anæsthesia the partial pressure of oxygen must be below 75 mm.[75, 76] and even as low as 66 mm.[77] Mice will live for 10–13 days in mixtures of 90% nitrous oxide–10% oxygen,[78] while as little as 3–4% of oxygen will support life in dogs.[79] Extreme asphyxia may set in if the proportion of oxygen in the inspired air falls below 12–15%.[80]

Nitrous oxide causes some degree of acidosis in the blood, although this is less than that caused by ether or chloroform.[81, 82] Prolonged anæsthesia may lead to serious cerebral degeneration, and nitrous oxide is more harmful in this respect than other anæsthetics.[83–86] The damage is intensified as the proportion of oxygen is reduced, but there may be severe destruction of the cerebral cortex after 100 hr. inhalation of a mixture of nitrous oxide and oxygen containing 20% of the latter, indicating that the effects are not due to asphyxia alone.[87] A nitrous oxide–oxygen mixture containing 20% of oxygen inhibited the oxygen consumption of rat-brain cortex slices but not of homogenates. There was some inhibition of anaerobic glycolysis and the electron–oxygen-transport system through the cytochromes is sensitive to nitrous oxide. It is, however, concluded that anæsthesia cannot be explained by metabolic inhibition of glucose oxidation or uncoupling of oxidative phosphorylation.[88, 89] Nor does the agent appear to cause significant changes in carbohydrate metabolism,[90] although the blood sugar level is increased by 35–50%.[91] It is interesting that, in common with other anæsthetics, nitrous oxide causes an increased destruction of protein in rabbits[92] and that rats fed on a protein-deficient diet are more easily anæsthetized than rats on a normal diet.[93] The maximum admissible number of inhalations of pure nitrous oxide is 1–2, since the third inhalation decreases the oxygen saturation of the alveolar air to such an extent that an actual oxygen deficiency may occur.[94] Nitrous oxide is rapidly absorbed from the peritoneal cavity, 100 ml. being absorbed in 2 hr. as against 80 hr. for the same volume of nitrogen.[95] The gas has been found useful for radiography of the peritoneal cavity and other body cavities.[96]

Toxic Effects of Nitrogen Compounds

NITRATES

Nitrate ion in drinking water supplies may cause methæmoglobinæmia, and an upper limit of 20 p.p.m. has been set in Minnesota.[97]

NITRITES

The median lethal dose for rabbits is 0·876 g./kg. body weight,[247] and the dose estimated for a man of 70 kg. is 2 g.[248] Death occurs in 0·5–3 hr. and the symptoms resemble those of cyanide poisoning.[248, 249] Several cases of fatal poisoning have occurred through the use of sodium nitrite in place of sodium chloride to season food. The intestines are reddish in colour and the body is found to contain much nitrate.[250, 251] Much of the blood hæmoglobin is converted to methæmoglobin.[247, 251, 252]

AZIDES

Exposure of mice to hydrazoic acid vapour at a concentration of 0·02 mg./l. for 3 hr. resulted in 100% mortality.[253] The minimum lethal dose to rats of sodium azide by injection is between 35 and 38 mg./kg. body weight.[254] Sodium azide is a central irritant causing hæmaturia, cardiac irregularities[255, 256] and lowering of the blood pressure.[257] Death appears to be caused by a gradual paralysis of the vasomotor system.[258] Azides are decomposed by the liver with the liberation of nitrogen.[242]

NITROUS OXIDE

The symptoms of poisoning by nitrous oxide have been described.[98] Degenerative lesions occur in the lungs which become more susceptible to silicosis.[99] The absorption spectrum of blood treated with nitrous oxide has been described.[100]

NITRIC OXIDE

Nitric oxide appears to be tolerable for 0·5 hr. at a concentration of 78 p.p.m., whereas 780 p.p.m. was rapidly fatal.[101] The maximum concentration tolerated without symptoms is stated to be 300 p.p.m.[102] Nitric oxide combines with the hæmoglobin of the blood to form methæmoglobin and then a compound of methæmoglobin with nitric oxide which is strongly acid.[103, 104] Carbon monoxide and nitric oxide act synergistically in causing the death of cats.[105]

NITROGEN DIOXIDE

Inhalation of concentrations of nitrogen dioxide greater than 100 p.p.m. for periods of 4 hr. per day has been found to lead to fatal results,[106] while exposure of rats to concentrations of 9–14 p.p.m. intermittently for a total period of 40–96 hr.

leads to severe inflammation of the respiratory tract.[107] Nitrogen dioxide is absorbed by and affects mainly the lower respiratory tract.[108, 109] There is some resemblance between the toxic effects of nitrogen dioxide and those of hydrogen sulphide.[110]

NITROGEN PENTOXIDE

Nitrogen pentoxide is a very toxic lung irritant, acute pulmonary œdema being produced by exposure to 1 p.p.m. for 4 hr. while about 16 p.p.m. for 4 hr. produced pulmonary hæmorrhage but no œdema. The toxic effects were not exerted via formation of nitric acid.[111]

NITROUS FUMES

A very serious potential industrial hazard is that due to nitrous fumes. This is the name given to a mixture of nitrous and nitric oxides, nitrogen dioxide, nitrogen pentoxide, etc., of variable composition which arises in many industrial processes or operations.[112, 113] Many countries have issued regulations which limit the maximum permissible concentration of nitrous fumes in the air of workrooms, and a figure of 10 p.p.m. is generally agreed as the limit for prolonged exposure.[114–117] Tests have been developed and simple apparatus designed to detect with accuracy the concentration of nitrous fumes in this range.[115, 118, 119] Automatic warning devices have also been produced.[120] Nitrous fumes are formed by modern explosives, the gases from which may contain 15–20% of N_2O.[121–123] Many accidents have been caused by the inhalation of nitrous fumes produced by electric arcs.[124, 125] From the kinetics of oxidation of nitric oxide it can be shown that the fumes from an electric arc contain mainly nitric oxide, but nitrogen dioxide may predominate under conditions of poor ventilation.[126] The concentration of nitric oxide has been found to vary from 200 to 1500 p.p.m., depending on the type of carbon electrodes and the power consumption.[127] The air around the rectifiers of an *X*-ray plant used for deep therapy was found to contain sufficient nitrogen dioxide to be a source of danger to operators and patients.[128] Toxic concentrations of nitrous fumes are readily produced during electric arc welding, particularly in confined spaces. Nitrogen dioxide is regarded as the most dangerous gas produced, being more toxic and attaining higher concentrations in practice than carbon monoxide.[129, 130] Open gas burners produce some nitrous fumes,[131] but a much more serious hazard is the operation of oxy-acetylene welding which may produce lethal concentrations of nitrous oxide in 15 min. in small unventilated spaces.[132] There is some correlation between the rate of production of nitrous fumes and the rate of burning of acetylene.[134] Nitrous fumes are among the toxic gases that may be produced at fires.[135, 136] Chemical works using pickling baths are a source of danger,[137–139] and two fatal cases of poisoning occurred among workers filling corn silos. 'Silo-filler's disease' is believed to be caused by nitrogen dioxide.[140] Dangerous concentrations of nitrous fumes have also been reported in spectral analytical laboratories,[141, 142] in motion picture projection rooms[143] and in gold or coal mines.[144] It has been found that up to 50 p.p.m. of nitric oxide may be produced by a bunsen burner burning with excess of air and larger amounts by a luminous flame.[145] Oxides of nitrogen have been identified in Los Angeles smog, which is believed to be produced partly by the oxidation of hydrocarbons by these oxides.[146–149]

The minimum lethal dose of a crude mixture of nitrous fumes produced by the action of nitric acid on copper is of the order of 1 g. per cu. m. for a 0·5 hr. exposure with dogs, rabbits, guinea pigs and rats.[150] Nitrous fumes, which are a common impurity in ozone, enhance its toxicity to bacteria and to higher organisms. The nitrous fumes are probably oxidized to nitrogen pentoxide, which is about three times as toxic as ozone itself.[151–153] Poisoning by nitrous fumes is marked by an elevation in the blood platelet count before other symptoms arise.[154] In addition to the well-known pulmonary inflammation[155] other striking symptoms have occasionally been reported, such as spastic paralysis involving the upper and lower extremities of one side,[156] pigmentation of finger-nails, defects of teeth enamel, bradycardia and a disturbed blood picture,[157] brain purpura and capillary cerebral hæmorrhages.[158] Methæmoglobin is formed in the blood on inhalation of nitrous fumes at concentrations above 0·01 μg. per litre,[1] this methæmoglobin being reduced by subsequent inhalation of fresh air.[159–161] A number of sensitive tests have been devised for the detection and estimation of nitrite and nitrate in blood and other tissues.[162, 163]

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NITROGEN COMPOUNDS AND ENZYMES OR PROTEINS

Both the oxidation of nitrous oxide to nitric oxide and the reverse reaction, in which nitric oxide is reduced to nitrous oxide, are promoted by enzymes occurring in yeast maceration juice.[1] Nitric oxide combines reversibly with oxidized horseradish peroxidase hæmatin,[2] with cytochrome *c*[3] and with cytochrome oxidase,[4] each compound showing definite and characteristic spectral absorption bands. Nitric oxide combines with hæmoglobin and readily displaces carbon monoxide from combination with hæmoglobin. The kinetics of these reactions have been discussed.[5–7] The compounds of nitric oxide with hæmocyanins are green pigments which have been crystallized.[8] The spectral absorption bands of the compounds of nitric oxide with hæmatins and various hæmoproteins have been described in detail.[9] Nitric oxide markedly weakens Rous sarcoma virus in the dark but light seems to inhibit the action.[10]

Irradiation of globin, gelatin and casein with ultra-violet light liberates ammonia which is believed to arise from the heterocyclic rings of histidine, proline and hydroxyproline.[11] By continued action of nitrous acid on proteins in the volumetric Van Slyke apparatus and measurement of the nitrogen released at different time intervals, it is possible to estimate the proportion of lysine in the protein.[12] There have been a number of studies of the action of nitrous acid on proteins and peptides under various conditions, and it has been shown that the various amino groups differ in their readiness to react with this acid.[13–15]

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